

## **Public Review Draft**

**September 24 1999**

### **Appendix 2**

#### **Photochemical Modeling**

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## 1. Introduction

This Section describes the air quality simulations performed in support of the analysis of the potential impact on air quality caused by the phase-out of gasoline containing methyl tert-butyl ether and replacement by ethanol-based or non-oxygenated gasoline fuels. A brief description of the air quality model is presented together with the photochemical mechanism chosen. A description of the input files necessary to run each of the scenarios considered is presented, together with a summary of the results. A discussion of model performance is included.

## 2. Flexible Chemical Mechanism Version of the Urban Airshed Model

Photochemical air quality models are a primary tool for understanding the complex interrelationships among pollutants emitted and transported in a given area. Photochemical air quality models are computer models that represent the state-of-the-science understanding of how ozone and other secondary pollutants are formed and their relationship to the primary pollutants emitted by different source categories. They have been used to assess the effectiveness of air pollution control strategies to achieve the air quality standards. The Flexible Chemical Mechanism Version of the Urban Airshed Model (UAM-FCM) is an air quality model that has been used by CARB since 1995.

The UAM-FCM is an adaptation of the Urban Airshed Model (UAM) to provide flexibility in incorporating different Carbon Bond IV or SAPRC-type photochemical mechanisms into the UAM (Kumar *et al.*, 1995). The UAM has been the primary air quality regulatory model for ozone control strategy development. However, it has a hard-coded Carbon Bond IV photochemical mechanism, together with a unique algorithm to solve the set of differential equations representing the chemical transformations that is accurate, robust and fast. The algorithm was designed to take maximum advantage of the Carbon Bond IV features. The treatment of photolytic reactions in the UAM is also unique. All values for the photolytic reaction rates are hard-coded, and depend on the value of the NO<sub>2</sub> photolytic reaction rate. The hard-coded approach in the UAM makes it very difficult to study recent and more updated mechanisms, such as those developed by Dr. W.P.L. Carter at the University of Riverside. Any change or update in the Carbon Bond IV mechanism, photolytic rates, or the implementation of a different chemical mechanism requires changes to the UAM code that need to be done by hand. The UAM-FCM, however, can read a text file version of a mechanism and create program subroutines that are readily integrated with the airshed model (Kumar *et al.*, 1995). Below we briefly describe the main aspects of the UAM and the UAM-FCM.

### 2.1 Urban Airshed Model

Morris and Meyers (1990) provide a detailed description of the UAM. Only a brief summary is provided here. The UAM is a gridded 3-dimensional air quality model that can simulate the atmospheric physical and chemical processes that cause air pollution. The basic equation is:

$$\frac{\partial C_i}{\partial t} + \frac{\partial(uC_i)}{\partial x} + \frac{\partial(vC_i)}{\partial y} + \frac{\partial(wC_i)}{\partial z} = \frac{\partial}{\partial x}(K_H \frac{\partial C_i}{\partial x}) + \frac{\partial}{\partial y}(K_H \frac{\partial C_i}{\partial y}) + \frac{\partial}{\partial z}(K_V \frac{\partial C_i}{\partial z}) + R_i + S_i + L_i \quad \text{Eqn.(1)}$$

The first term on the left of Eqn.(1) represents the time-varying concentration of pollutant  $i$ , and the last three terms on the left side of Eqn.(1) represent advection. The first three terms on the right side of Eqn.(1) represent turbulent diffusion,  $R_i$  are chemical processes,  $S_i$  are emission processes, and  $L_i$  correspond to pollutant sinks. The other terms in Eqn.(1) are

$$\begin{array}{ll} u,v,w & = \text{horizontal and vertical speed wind components} \\ K_H, K_V & = \text{horizontal and vertical turbulent coefficients} \end{array}$$

Eqn.(1) is solved for each pollutant and grid cell at each time step in the simulation. As designed, the UAM has hard-coded the Carbon Bond IV (CB4) chemical mechanism. The CB4 version implemented in the UAM was last updated in 1993 by adding radical-radical interactions. As stated before, the hard-coded approach to the atmospheric chemical mechanism used in the UAM prevents the implementation of newer and more up-to-date chemical mechanisms.

## 2.2 UAM-FCM

The UAM-FCM was developed under contract for CARB (Kumar *et al.*, 1995). The UAM-FCM has a software package (the FCM) that reads a text file describing the photochemical mechanism, and creates a set of mechanism-specific programs that are then integrated into the UAM. The FCM allows the user to incorporate reaction specific photolysis rates, by providing a file for each photolytic reaction, with data on cross section and quantum yield for each wavelength of interest. The UAM-FCM has a generalized technique to solve the set of differential equations that is not mechanism specific, but is accurate and robust. The current version of the UAM-FCM can handle up to 220 chemical reactions (including up to 20 photolytic reactions), and up to 140 chemical species.

## 3. SAPRC97

Carter (Carter *et al.*, 1993 and 1997) developed the atmospheric chemical mechanism designated as SAPRC97 (version D), which is readily processed by the UAM-FCM software. To save computing time in solving the set of differential equations that represent the reaction mechanism, only a small number of hydrocarbon species are treated explicitly in this mechanism. In SAPRC, hydrocarbons are grouped together using the lumped-molecule approach. In this approach the reactions of many alkanes, alkenes, and aromatic species that are present in the emissions inventory are represented by lumped reaction mechanisms (Carter, 1990). The computer software calculates the kinetic rates and product yield parameters for the lumped species that best represent the unique hydrocarbon mixture in the emissions inventory (Carter, 1988, 1990). For this study the one-product mechanism is used to represent the reactions of isoprene (Carter, 1996). In addition, explicit reaction mechanisms (as opposed to a lumped representation) for several compounds of interest (such as benzene, 1,3 butadiene, ethanol, and methyl-tert-butyl ether) were added to the original version of the SAPRC97. It was also desired to distinguish between acetaldehyde and formaldehyde formed as by-products of photochemical reactions (secondary), from those emitted directly from sources (primary). The explicit reactions for the additional species were obtained from Dr. Carter's ftp site (<ftp://cert.ucr.edu/pub/carter/mech/saprc97>).

A complete listing of this photochemical mechanism is provided in Attachment A. The list of hydrocarbon species that are treated explicitly is given in Table 1. In addition to the species listed in Table 1, the photochemical mechanism includes a large number of species that are generated by the oxidation of hydrocarbons, as well as a set of chemical reactions that represents the inorganic reactions that take place in air. The mechanism used in our simulations has a total of 99 species and 204 reactions, of which 20 are photolytic. Of the 99 species, 29 are treated as steady state, 4 species are held constant, and hourly average concentrations are generated by the UAM-FCM for the other 66 species.

**Table 1**  
**List of Hydrocarbon Species Treated explicitly in SAPRC97**

Name	Symbol
Formaldehyde (secondary)	HCHO
Formaldehyde (primary)	FORM
Acetaldehyde (secondary)	CCHO
Acetaldehyde (primary)	ALD
Acetone	ACET
Methyl ethyl ketone	MEK
Peroxy acetyl nitrate	PAN
Peroxy propionyl nitrate	PPN
Methane	CH4
Ethene	ETHE
Isoprene	ISOP
Benzene	C6H6
1,3-butadiene	BUTD
p-dichlorobenzene	PDCB
Perchloroethylene	PERC
Dichloromethylene	DICM
Ethanol	ETOH
Methyl tert-butyl ether	MTBE
Glyoxal	GLY
Methyl Glyoxal	MGLY
Benzaldehyde	BALD
Cresols	CRES
Phenols	PHEN

#### 4. Computer Used

The executable UAM-FCM files were prepared and compiled according to the recommended procedure (Kumar *et al.*, 1995). The emissions inventory corresponding to each year and case under study were used to calculate the reaction rates and product yields of the lumped species. All simulations were run on a Unix workstation. The time to run a 24-hr episode simulation was about 2 hours and twenty minutes.

#### 5. Episode and Domain

The UAM-FCM was applied to a three-day summer ozone episode in the South Coast, the August 26-28, 1987 SCAQS episode. The SCAQS domain has been gridded into 65 X 40 x 5 cells. Each horizontal square cell is 5 x 5 km<sup>2</sup>, with varying vertical height. The origin of the domain is at (275, 3670) in UTM coordinates (Zone 11). The domain is shown in Figure 1. It includes the counties of Los Angeles, Orange, and Kern, and portions of Riverside, San Diego, San Bernardino, and Ventura counties.

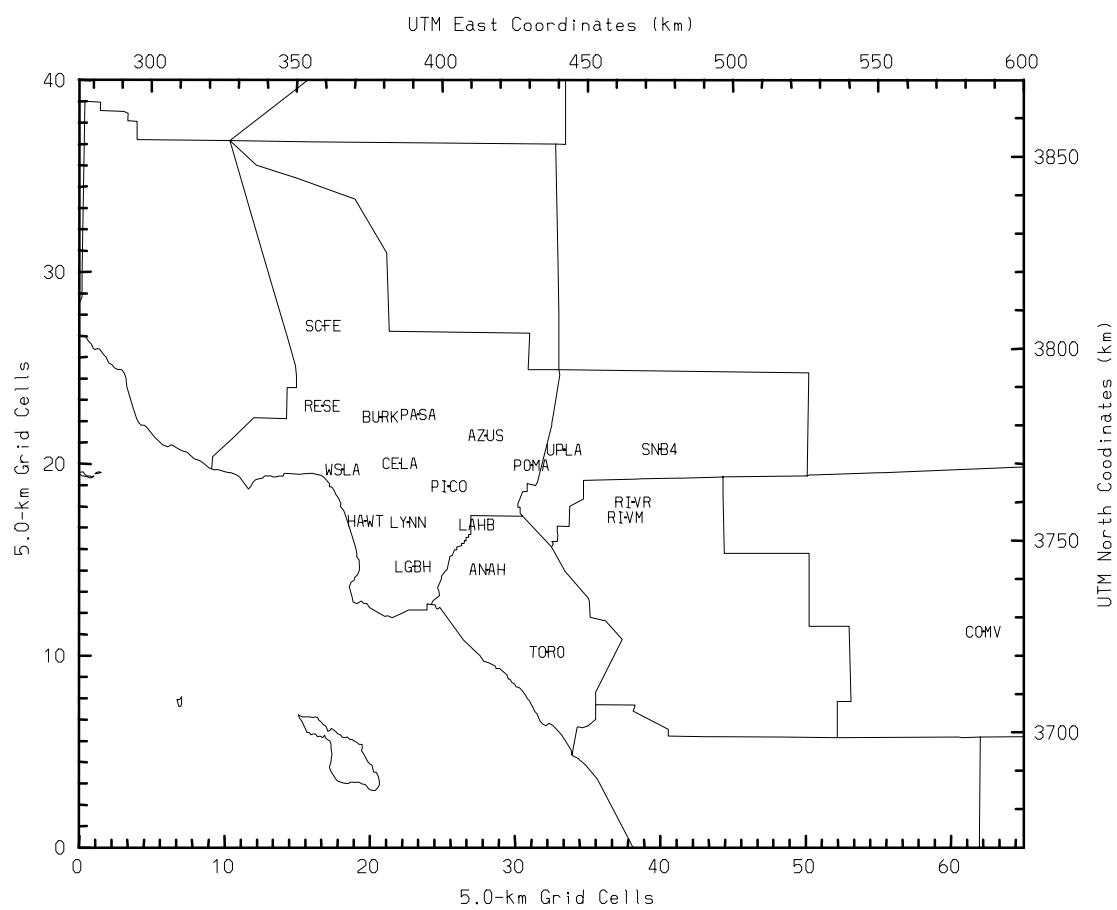


Figure 1. Modeling Domain

## **6. Basic Input files**

The UAM-FCM requires 13 input files that provide information on the initial and boundary conditions of the domain, temperature, wind direction, wind speed, terrain, photolysis rates, reaction rate constants and product yields, and emissions from area and point sources. Mobile sources and biogenic emissions are included in the area source file. The files used in our simulations, (except for the initial and boundary conditions, and area and point source emissions) were prepared by the South Coast Air Quality Management District for the 1994 State Implementation Plan (SCAQMD, 1994). The same diffusion break, region top, metscalars, terrain, temperature and meteorological input files were used in all simulations, since these characterize the meteorological conditions for the episode and terrain. Table 2 provides a description of these files. Other files, such as initial and boundary conditions, point sources and area emissions were created for each specific simulation.

**Table 2**  
**List of the Meteorological and Terrain files**  
**For SCAQS August 26-28, 1987 Episode**

Input File identification	Description
ms238d11.b, ms239d11.b, ms240d11.b	Metscalar file
sim238bl, sim239bl, sim240bl	Control file
df238d11.b	Diffusion break file
tm238d11.b, tm239d11.b, tm240d11.b	Temperature file
rt238d11.b	Region top file
tr238d11.b	Terrain file
wd238d11.b, wd239d11.b, wd240d11.b	Wind file

## **7. Region Top and Boundary Conditions**

The region top and boundary conditions (together with the point and area sources) are specific to each of the different scenarios considered in this modeling study. The scenarios considered include the years 1997 and 2003 with different types of gasoline. These scenarios are listed in Table 3.

**Table 3**  
**Scenarios Considered for the**  
**MTBE Phaseout Study**

Scenario	Description of Motor Vehicle Fuel Used
1997	Current MTBE-based Cleaner-Burning Gasoline
2003/mtbe	Year 2003 with MTBE-based Cleaner-Burning Gasoline
2003/et20	Year 2003 with Ethanol-based fully complying fuel (with oxygen content of 2.0%)
2003/et35	Year 2003 with Ethanol-based fully complying fuel (with oxygen content of 3.5%)
2003/unox	Year 2003 with a non-oxygenated fully complying fuel
2003/et20h	Year 2003 with Ethanol-based fully complying fuel (with oxygen content of 2.0%). Used headspace factors recommended by Dr. Robert Harley, and the resultant fuel profile was applied to hot soaks and running evaps
2003/et35h	Year 2003 with Ethanol-based fully complying fuel (with oxygen content of 3.5%). Used headspace factors recommended by Dr. Robert Harley, and the resultant fuel profile was applied to hot soaks and running evaps

The region top and boundary condition files describe the air quality at the boundaries of the domain under study. These two files specify hourly ambient levels of each of the species in the SAPRC mechanism. For these simulations the region top and boundary conditions were treated as constant for all species throughout the episode. Region top concentrations were essentially the same as those used for the boundary conditions. Table 4 and Table 5 show the pollutant concentrations used for the boundary and region top, respectively.

**Table 4**  
**Boundary Baseline Concentration**  
**(ppb)**

Species	1997	2003/et20	2003/et35	2003/mtbe	2003/unox
O3	40.0	40.0	40.0	40.0	40.0
NO	0.9095	0.8285	0.8285	0.8285	0.8285
NO2	1.6832	1.4	1.4	1.4	1.4
N2O5	1.0	1.0	1.0	1.0	1.0
HONO	0.08371	0.06913	0.06913	0.06913	0.06913
CO	200.0	200.0	200.0	200.0	200.0
CO2	1000.0	1000.0	1000.0	1000.0	1000.0
CCHO	0.5	0.53	0.53	0.53	0.53
HCHO	0.5	0.5	0.5	0.5	0.5
RCHO	0.98	0.98	0.98	0.98	0.98
ETHE	0.829	0.7626	0.7626	0.7626	0.7626
CH4	1720.0	1720.0	1720.0	1720.0	1720.0
ALK1	0.49	0.49	0.49	0.49	0.49
ALK2	1.01	1.01	1.01	1.01	1.01
ARO1	0.4273	0.3962	0.3962	0.3962	0.3962
ARO2	0.14507	0.13538	0.13538	0.13538	0.13538
OLE1	0.7048	0.69056	0.69056	0.69056	0.69056
OLE2	0.01	0.01	0.01	0.01	0.01
C6H6	0.08	0.08	0.08	0.08	0.08
NO3	1.0	1.0	1.0	1.0	1.0
HO2	0.1	0.1	0.1	0.1	0.1
MTBE	0.1	0.01	0.01	0.1	0.01
ETOH	0.01	0.3	0.41	0.01	0.01
All other species	0.01	0.01	0.01	0.01	0.01

**Table 5**  
**Region Top Concentrations**  
**(ppb)**

Species	1997	2003/et20	2003/et35	2003/mtbe	2003/unox
O3	40.0	40.0	40.0	40.0	40.0
NO	0.9095	0.8285	0.8285	0.8285	0.8285
NO2	1.6832	1.4	1.4	1.4	1.4
N2O5	1.0	1.0	1.0	1.0	1.0
HONO	0.08371	0.06913	0.06913	0.06913	0.06913
CO	200.0	200.0	200.0	200.0	200.0
CO2	1000.0	1000.0	1000.0	1000.0	1000.0
CCHO	0.5	0.53	0.53	0.53	0.53
HCHO	0.5	0.5	0.5	0.5	0.5
RCHO	0.98	0.98	0.98	0.98	0.98
ETHE	0.829	0.7626	0.7626	0.7626	0.7626
CH4	1720.0	1720.0	1720.0	1720.0	1720.0
ALK1	0.49	0.49	0.49	0.49	0.49
ALK2	1.0	1.0	1.0	1.0	1.0
ARO1	0.4218	0.3912	0.3912	0.3912	0.3912
ARO2	0.14507	0.13538	0.13538	0.13538	0.13538
OLE1	0.7048	0.69056	0.69056	0.69056	0.69056
OLE2	0.01	0.01	0.01	0.01	0.01
C6H6	0.08	0.08	0.08	0.08	0.08
NO3	1.0	1.0	1.0	1.0	1.0
HO2	0.1	0.1	0.1	0.1	0.1
MTBE	0.1	0.01	0.01	0.1	0.01
ETOH	0.01	0.3	0.41	0.01	0.01
All other species	0.01	0.01	0.01	0.01	0.01

## 8. Initial Conditions

All simulations were started with the same initial conditions given in Table 6. Because of this, only the results of the last simulation day, August 28, are used in the analysis. The results of the last simulation day are insensitive to the initial conditions.

**Table 6**  
**Initial Species Concentrations**  
**(ppb)**

Species	Concentration
O3	70.0
NO	1.0
NO2	2.0
HNO3	0.1
HONO	0.1
CO	200.0
CO2	0.1
H2O2	0.1
CCHO	1.1
HCHO	5.8
RCHO	0.98
ETHE	1.4
CH4	1720.0
ALK1	0.49
ALK2	1.01
ARO1	0.7
ARO2	0.23
OLE1	0.83
OLE2	0.23
OLE3	0.00
C6H6	0.16
All other species	0.01

## 9. Point and Area Sources

Point source emission and area source emission files were prepared for each specific scenario studied. The preparation of each file is discussed elsewhere in this report.

## 10. Sites

Table 7 lists the 20 sites in the South Coast modeling domain used to analyze the results of each different scenario studied. In addition to these sites, the domain peak was also used. Figure 1 shows the site locations in the domain.

**Table 7**  
**Sites in the Modeling Domain**  
**Used to Study the Impact of Each of the Scenarios**  
**Studied.**

Site Name	Id
Anaheim	ANAH
Azusa	AZUS
Burbank	BURK
Los Angeles North Main	CELA
Costa Mesa -Mesa Verde Drive	COMV
Hawthorne	HAWT
La Habra	LABH
North Long Beach	LGBH
Lynwood	LYNN
Pasadena -S. Wilson Avenue	PASA
Pico Rivera	PICO
Pomona	POMA
Reseda	RESE
Riverside - Rubidoux	RIVR
Riverside -Magnolia	RIVM
Santa Clarita -County Fire Station	SCFE
San Bernardino -4 <sup>th</sup> Street	SNB4
El Toro	TORO
Upland	UPLA
West Los Angeles -VA Hospital	WSLA

## 11. Results

As indicated above, only the results of the third day of the episode simulated (August 28) were used in the analysis to avoid dependence on the initial conditions. Table 8 shows the domain peak concentration of the pollutants of interest for each scenario simulated. As shown in Table 8, the domain peak ozone slightly decreases (4.0 - 6.7%) from 1997 to 2003 because of reductions in overall emissions. CO shows a more significant decrease (27 - 35 %). Nitric acid decreases by up to 9.5%. In general the predicted concentrations do not show a large change from 1997 to 2003 for most of the pollutants, except for NO, NO<sub>2</sub>, CO, ethanol and nitric acid.

Among the year 2003 simulations, the et35 and et35h show the lowest peak ozone concentrations (220.1 and 221.2 ppb respectively), while the Unox case shows slightly higher peak ozone concentration (226.6 ppb). Note also that the CO concentration is higher for the Unox scenario among the year 2003 simulations, and is lowest for the Et35 and Et35h scenarios. The use of oxygenated fuels results in lower CO and hydrocarbon emissions, compared to the non-oxygenated gasoline. Therefore, as shown in Table 9, it is expected that the simulations using oxygenated gasoline will result in lower predicted ozone and CO concentrations.

**Table 8**  
**Domain Hourly Peak Concentrations**  
**Using Emissions for Each Scenario Considered**

Simulation	Domain Peak (ppb)							
	O3	CO	Formaldehyde <sup>6</sup>	Acetaldehyde <sup>6</sup>	C6H6	PAN	PPN	HNO3
<b>1997</b>	235.9	3023.6	22.7	9.2	3.4	4.4	1.4	57.7
<b>2003</b>								
Et20 <sup>1</sup>	224.2	2189.3	22.8	8.8	2.2	4.4	1.4	52.4
Et35 <sup>2</sup>	221.1	1968.2	22.9	8.9	2.3	4.4	1.4	52.2
Mtbe <sup>3</sup>	222.9	2189.1	23.1	8.7	2.2	4.2	1.4	52.3
Unox <sup>4</sup>	226.6	2262.9	22.8	8.8	2.2	4.4	1.5	52.5
Et20h <sup>5</sup>	222.5	2189.2	22.8	8.8	1.9	4.2	1.4	52.4
Et35h <sup>5</sup>	220.1	1968.1	22.9	8.9	2.0	4.2	1.4	52.2

1. et20 = ethanol-based fully complying fuel (with oxygen content of 2.0%)
2. et35 = ethanol-based fully complying fuel (with oxygen content of 3.5%)
3. mtbe = current MTBE-based cleaner burning gasoline
4. unox = non-oxygenated fully complying fuel
5. Harley sensitivity runs (labeled h) differ from et20 and et35 in that Harley's headspace calculations derived fuel profile was used for hot soaks and running evaps.
6. formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation

Figures 2-6 show hourly ozone, NO, and NO<sub>2</sub> for August 26 - 28, 1987 at Anaheim (ANAH), Burbank (BURK), downtown Los Angeles (CELA), Riverside-Rubidoux (RIVR), and at the domain maximum (GMX). The time plots clearly show that the 1997 and 2003 scenarios have very similar predicted ozone concentrations during the last day of the simulation. There are significant differences in predicted NO<sub>2</sub> concentrations between 1997 and 2003, as expected. All 2003 scenarios have the essentially the same predicted NO and NO<sub>2</sub> hourly concentrations.

Figures 7-11 show MTBE, ETOH, and CO time series plots for August 26 - 28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain peak. The plots are only for the 2003 scenarios (Et20, Et35, Unox, and Mtbe). As expected the 2003/Et35 scenario has highest predicted ethanol concentrations, while the 2003/mtbe is the only scenario with significant MTBE hourly concentrations among all the 2003 scenarios.

Figures 12-16 show time series plots of hourly PAN, PPN, and HNO<sub>3</sub> concentrations for August 26 - 28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain peak. Predicted PAN, PPN, and HNO<sub>3</sub> concentrations are all scenarios. Both PAN and PPN show a large peak on the second day of the episode that has significantly decreased by the third day of the episode simulated.

From Figures 2-6, it is clear that although hydrocarbon and NOx emissions decreased from 1997 to 2003, the reduction did not significantly impact the radical flux levels predicted by the photochemical mechanism. This is confirmed by the small impact on the predicted peak ozone concentrations. In addition, the NOx-to-Hydrocarbon ratio may not have significantly changed from 1997 to 2003, which may explain the essentially similar PAN, PPN, and HNO<sub>3</sub> predicted concentrations for these years (see figures 12-16).

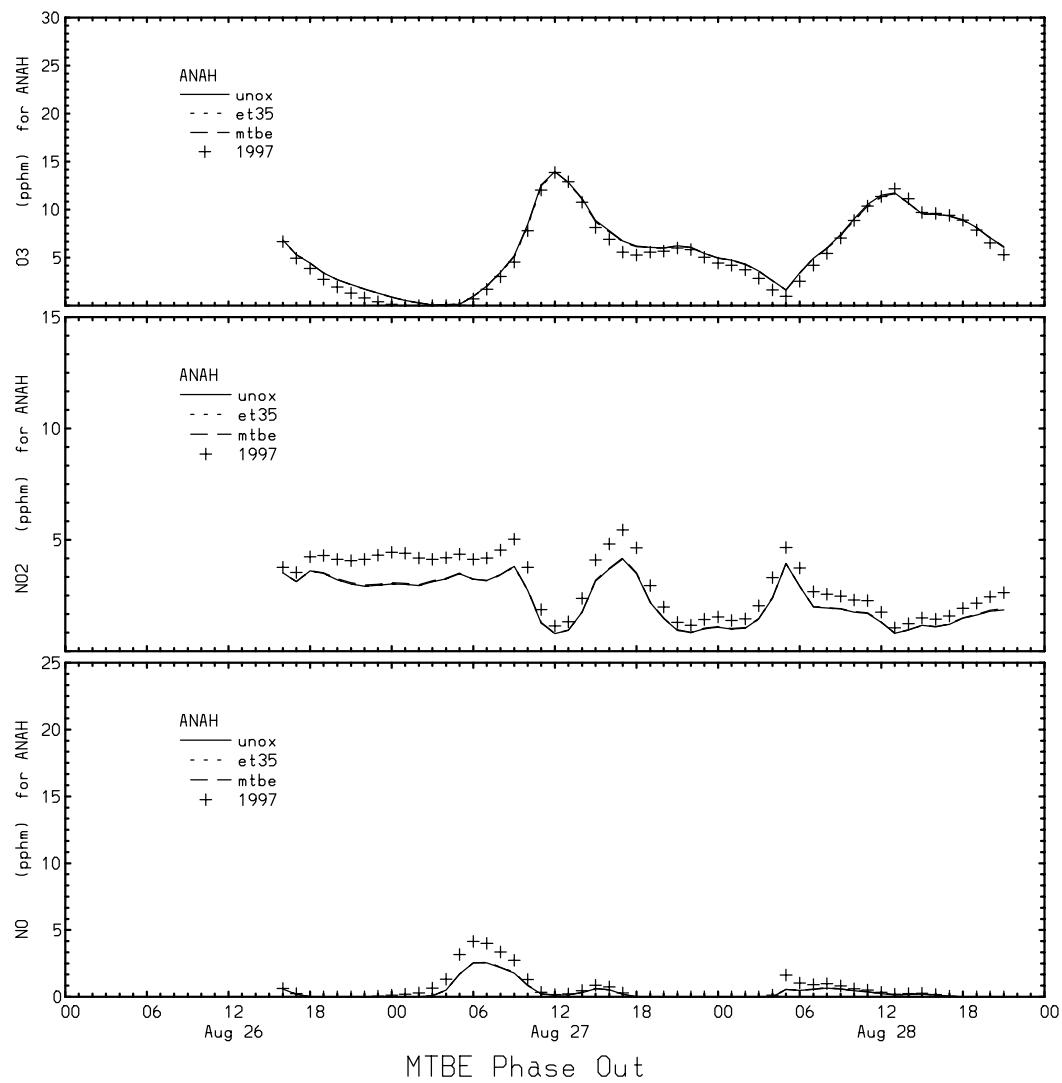


Figure 2. Time Series for Ozone, NO<sub>2</sub>, and NO at Anaheim for 1997 and 2003 Scenarios

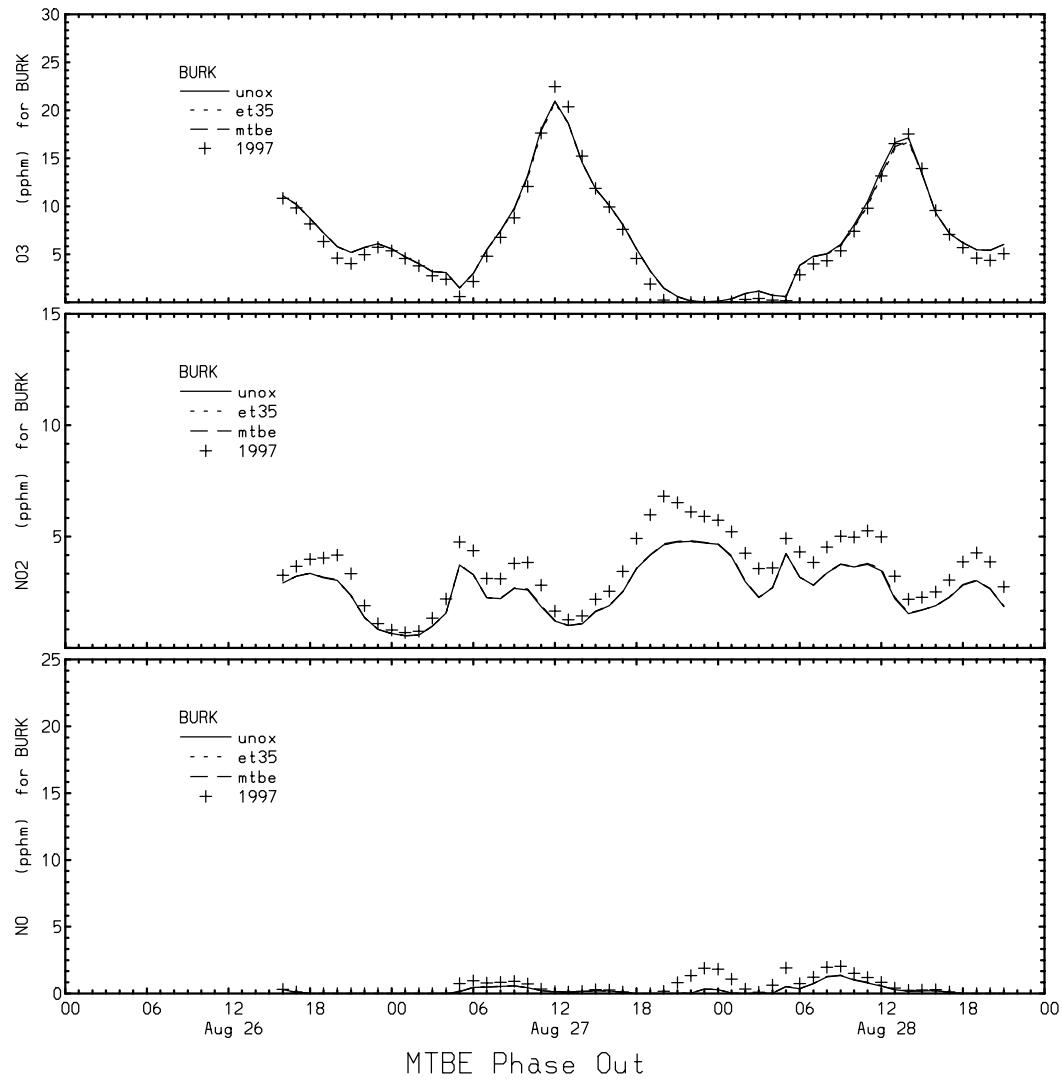


Figure 3. Time Series for Ozone, NO<sub>2</sub>, and NO at Burbank for 1997 and 2003 Scenarios

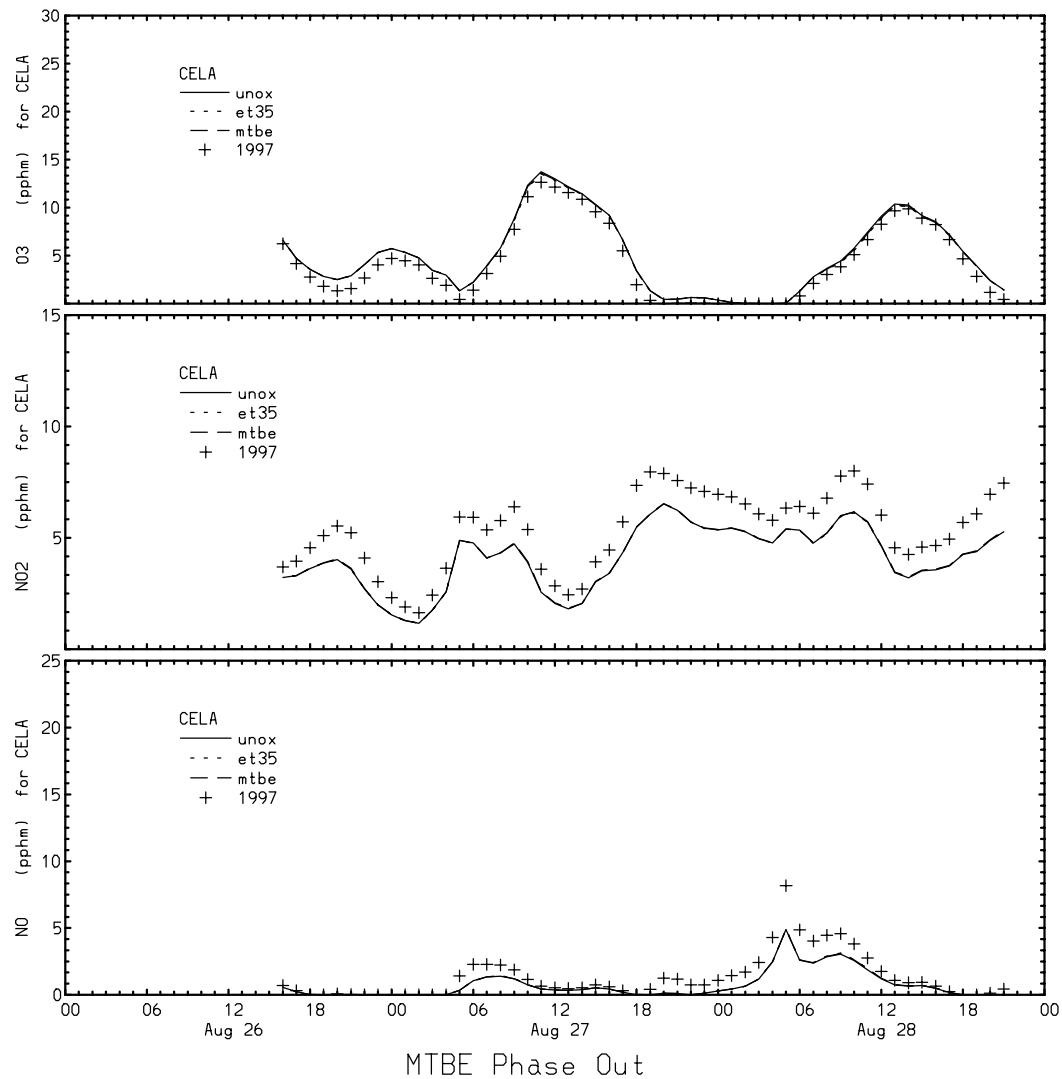


Figure 4. Time Series for Ozone, NO<sub>2</sub>, and NO at Los Angeles for 1997 and 2003 Scenarios

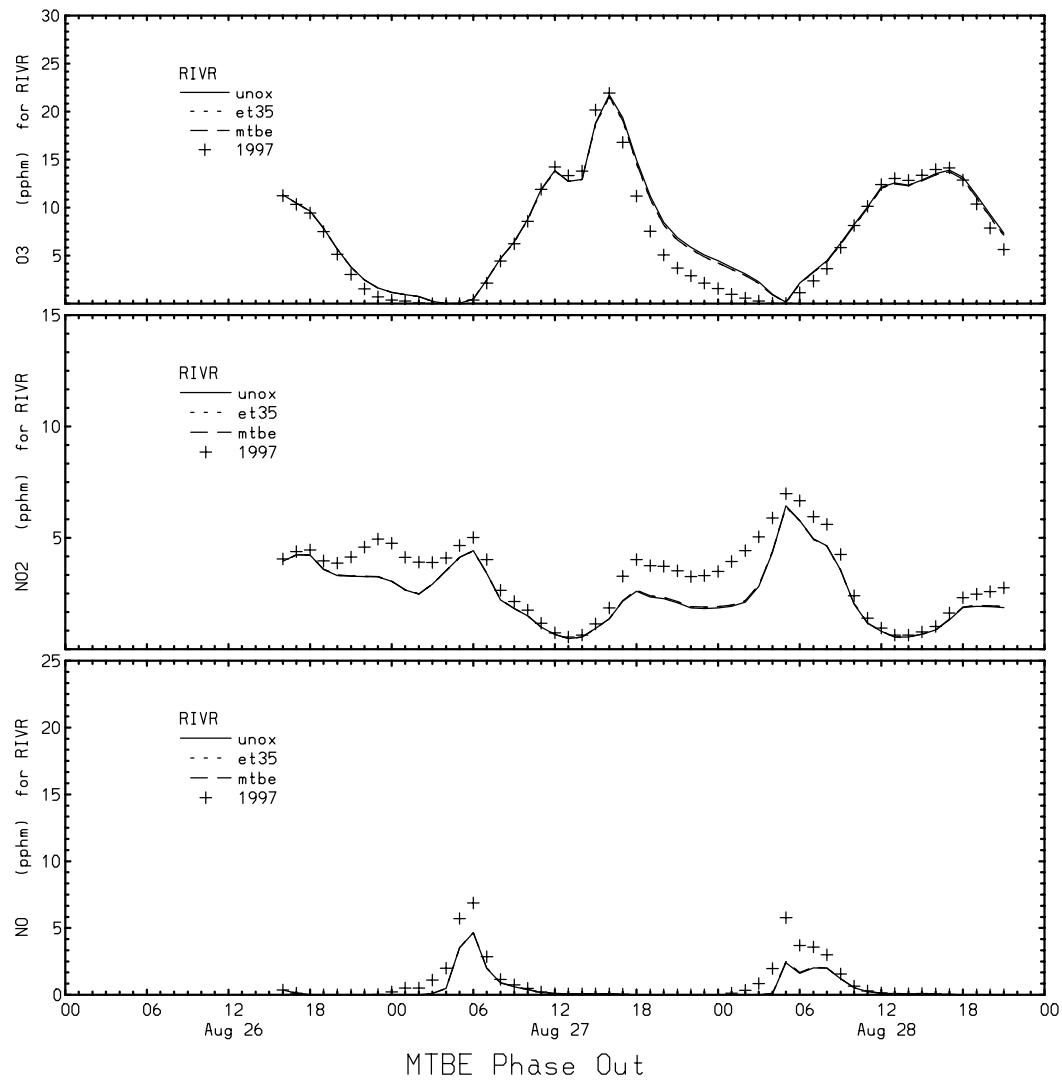


Figure 5. Time Series for Ozone, NO<sub>2</sub>, and NO at Riverside for 1997 and 2003 Scenarios

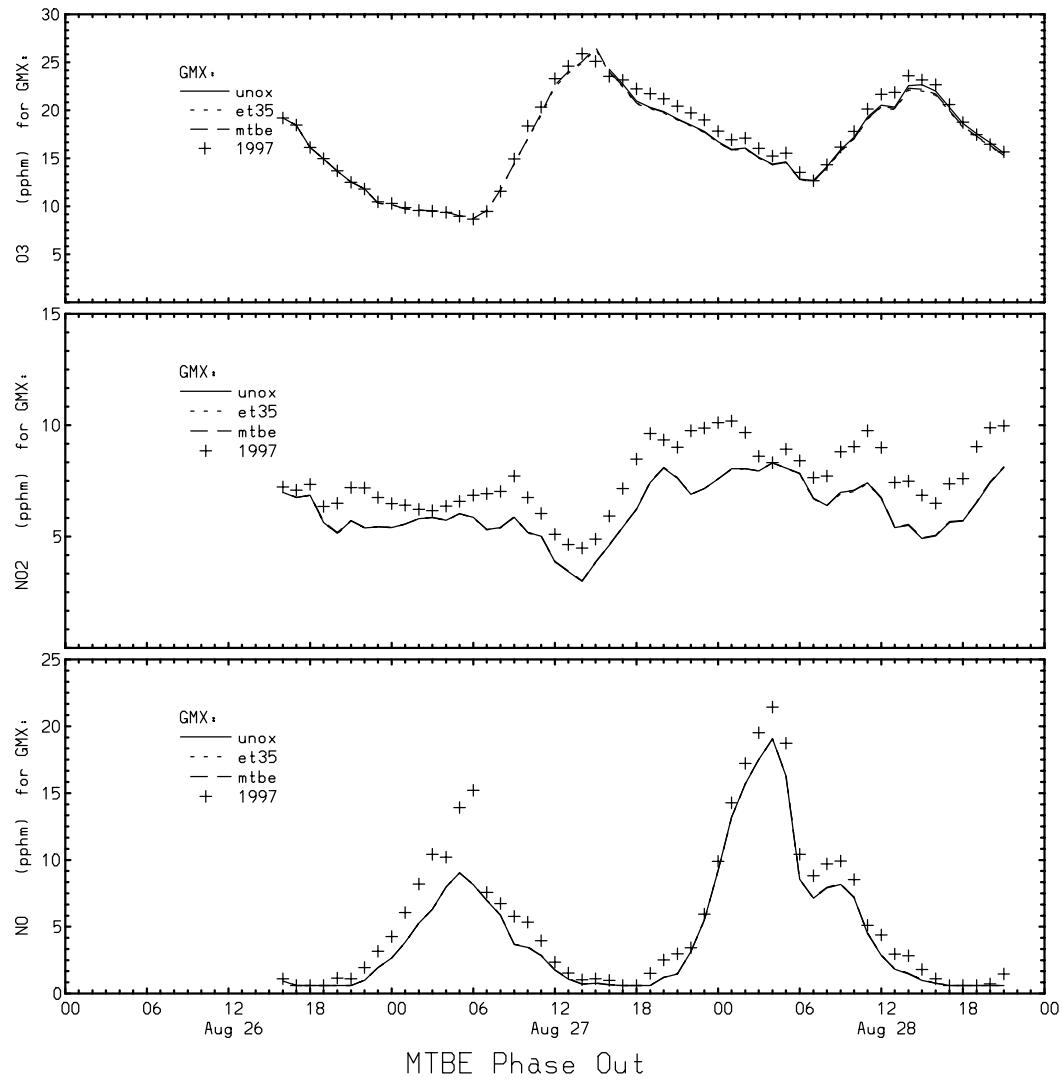


Figure 6. Time Series for Domain Maximum Ozone, NO<sub>2</sub>, and NO for 1997 and 2003 Scenarios

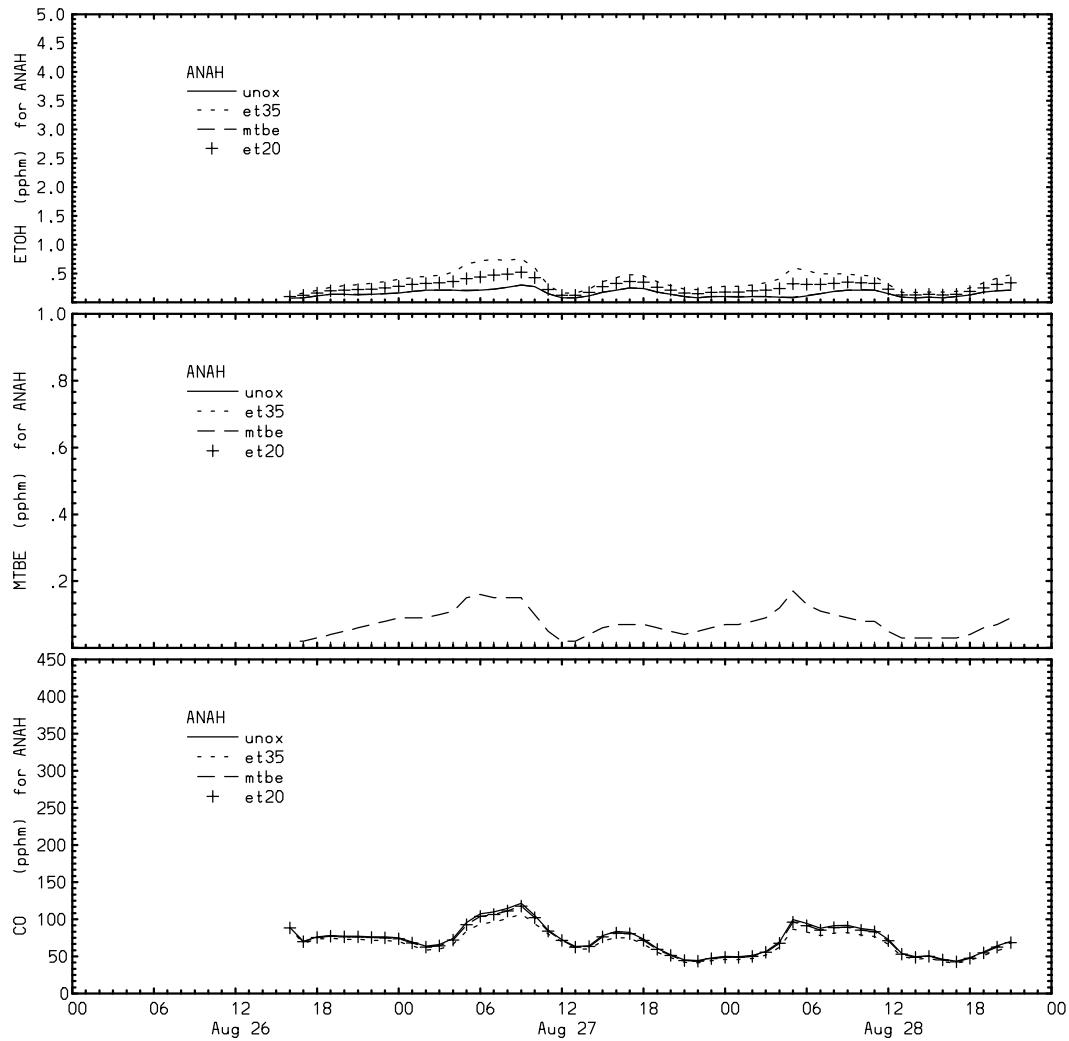


Figure 7. Time Series for MTBE, ETOH and CO at Anaheim for 2003 Scenarios

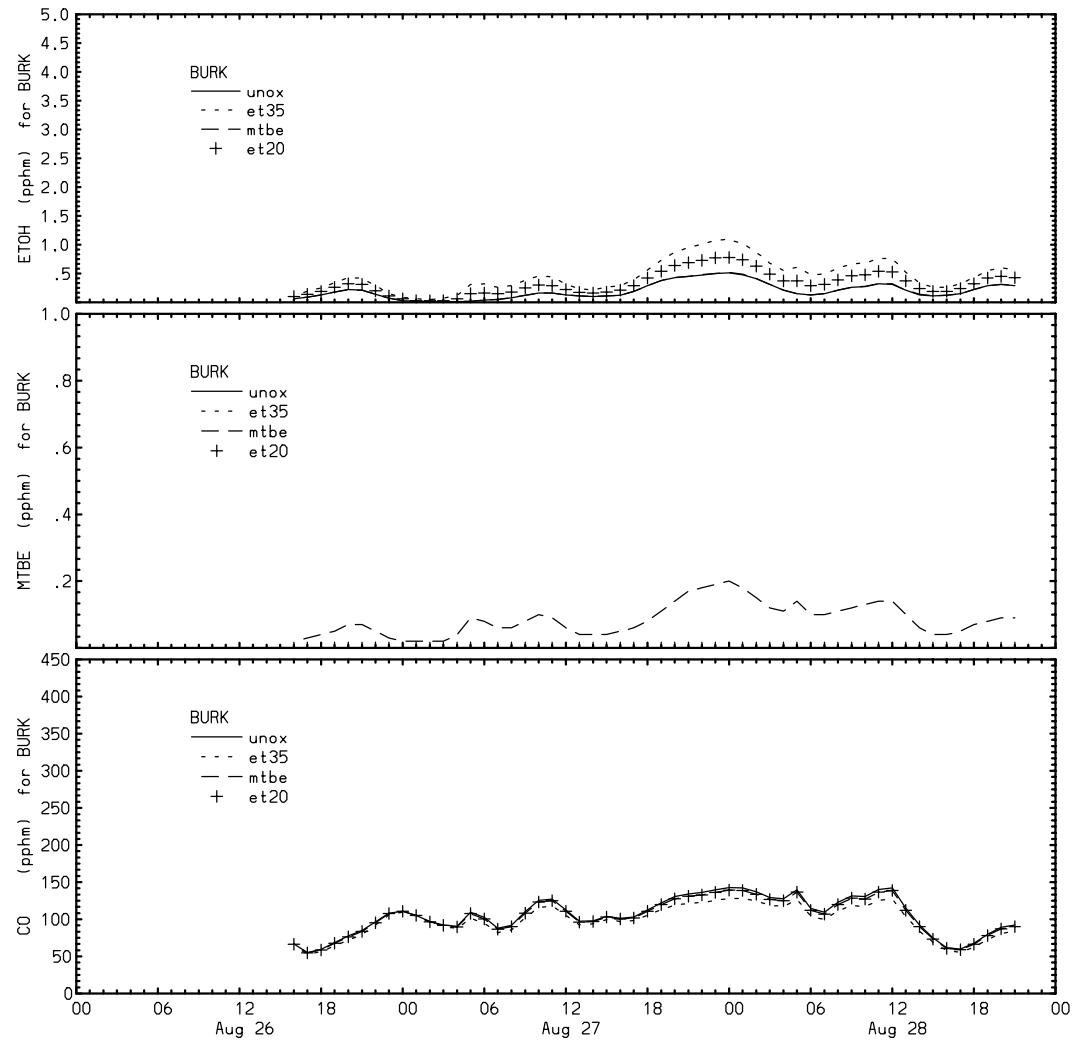


Figure 8. Time Series for MTBE, ETOH and CO at Burbank for 2003 Scenarios

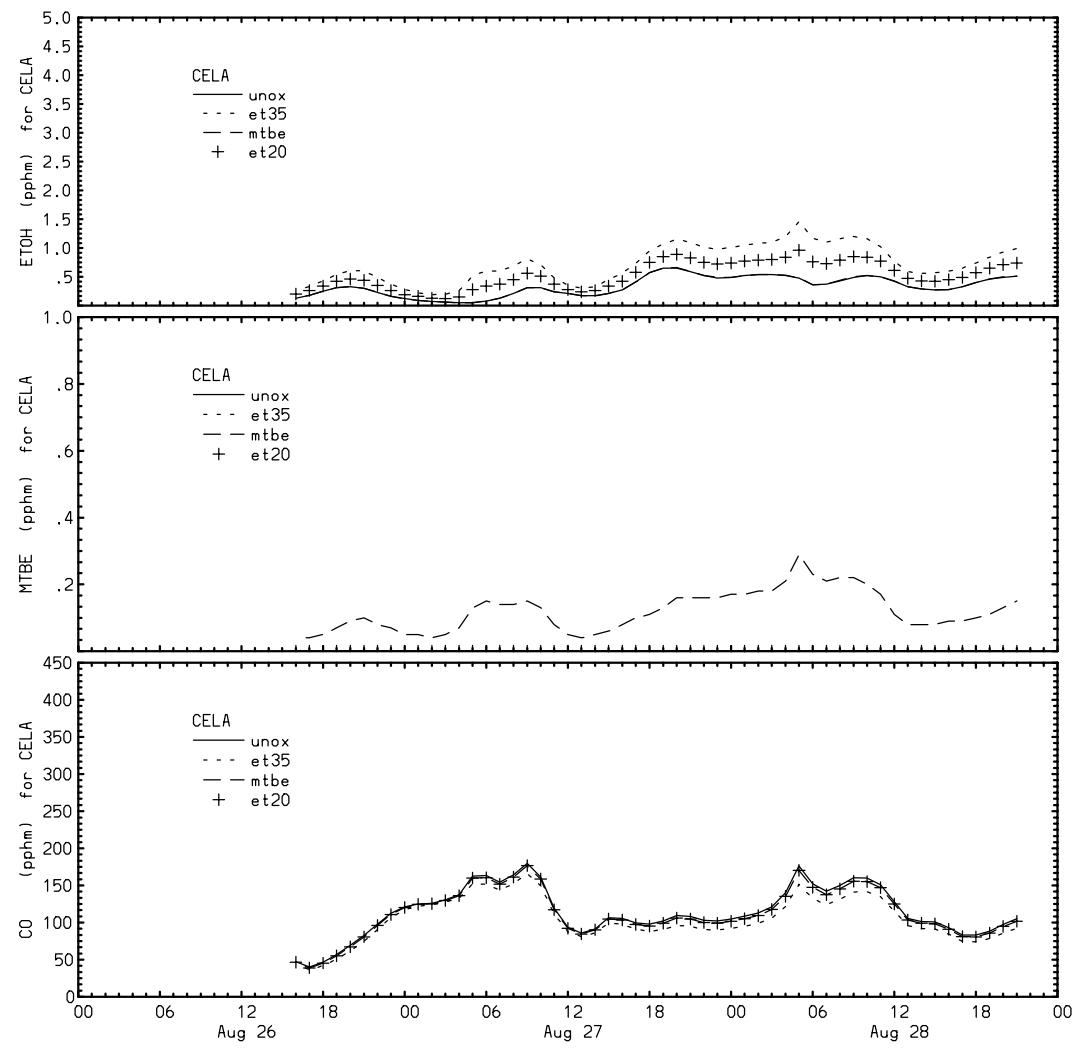


Figure 9. Time Series for MTBE, ETOH and CO at Los Angeles for 2003 Scenarios

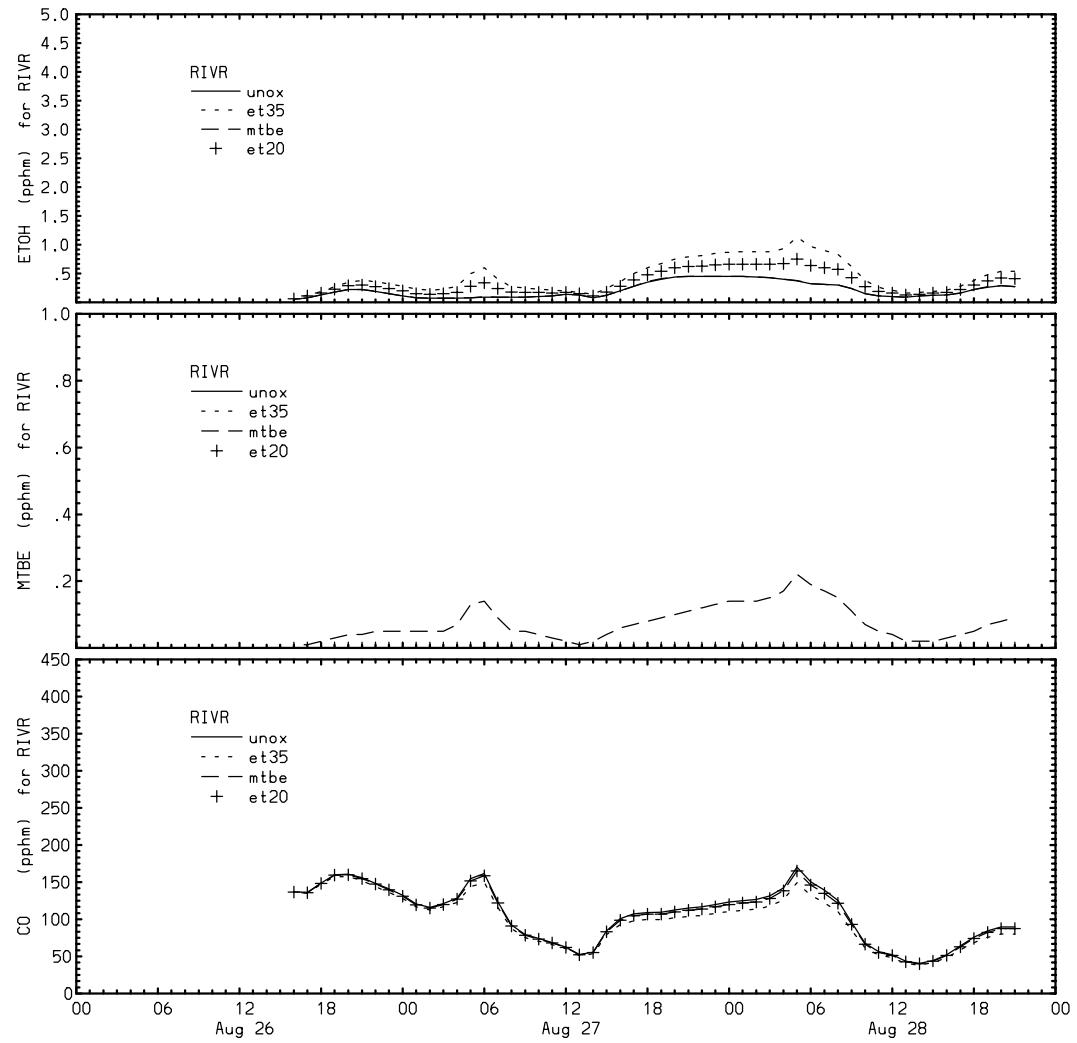


Figure 10. Time Series for MTBE, ETOH and CO at Riverside for 2003 Scenarios

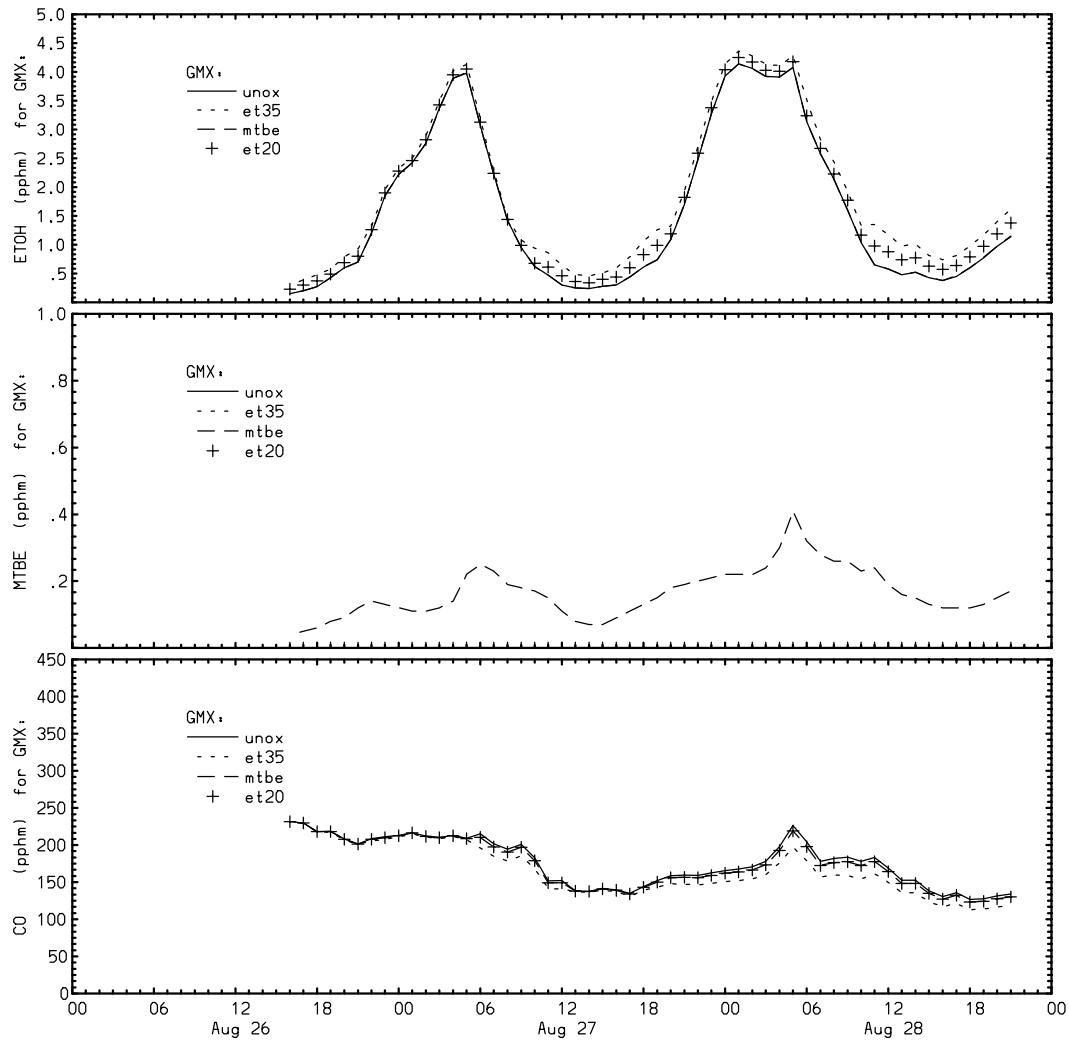


Figure 11. Time Series for Domain Maximum MTBE, ETOH and CO for 2003 Scenarios

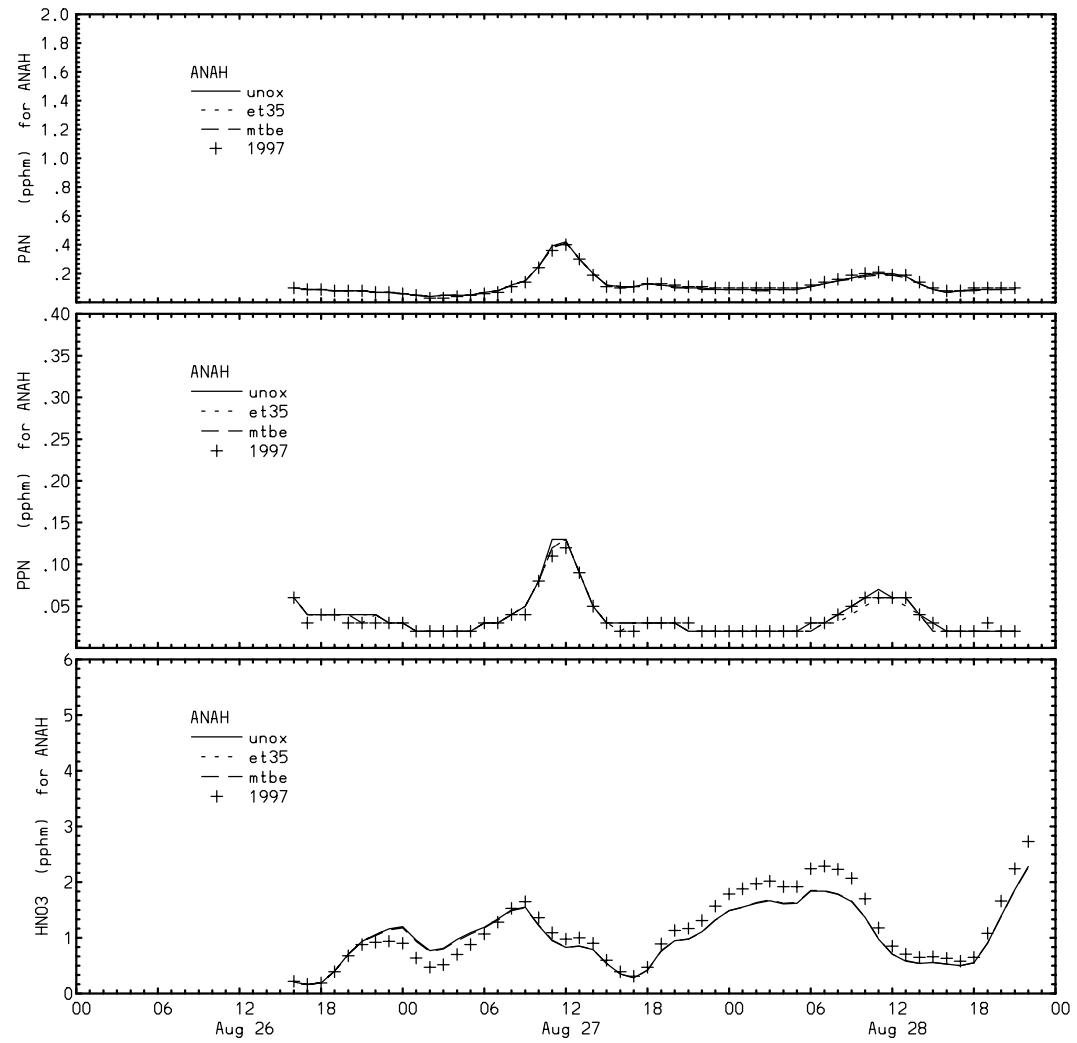


Figure 12. Time Series for PAN, PPN and HNO<sub>3</sub> at Anaheim for 1997 and 2003 Scenarios

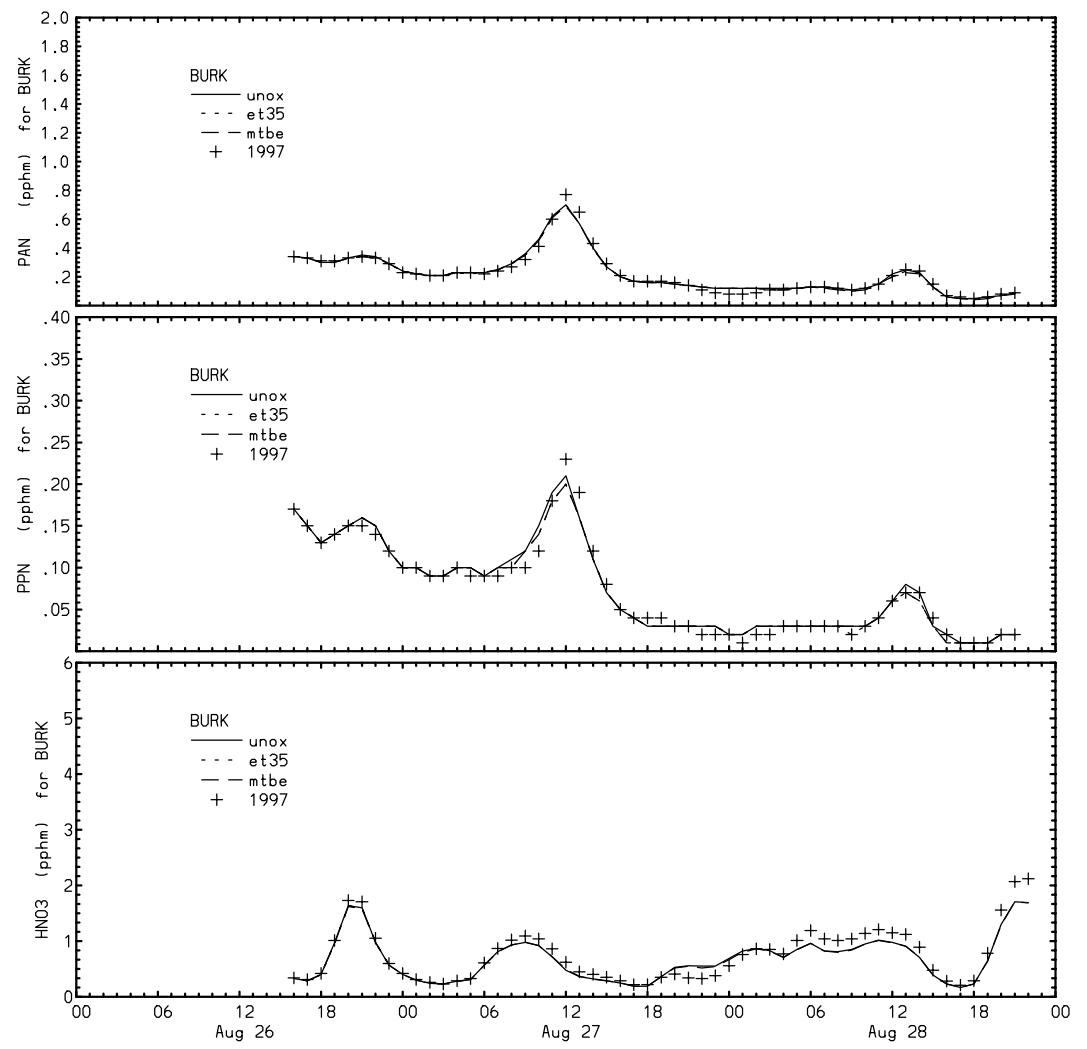


Figure 13. Time Series for PAN, PPN and HNO<sub>3</sub> at Burbank for 1997 and 2003 Scenarios

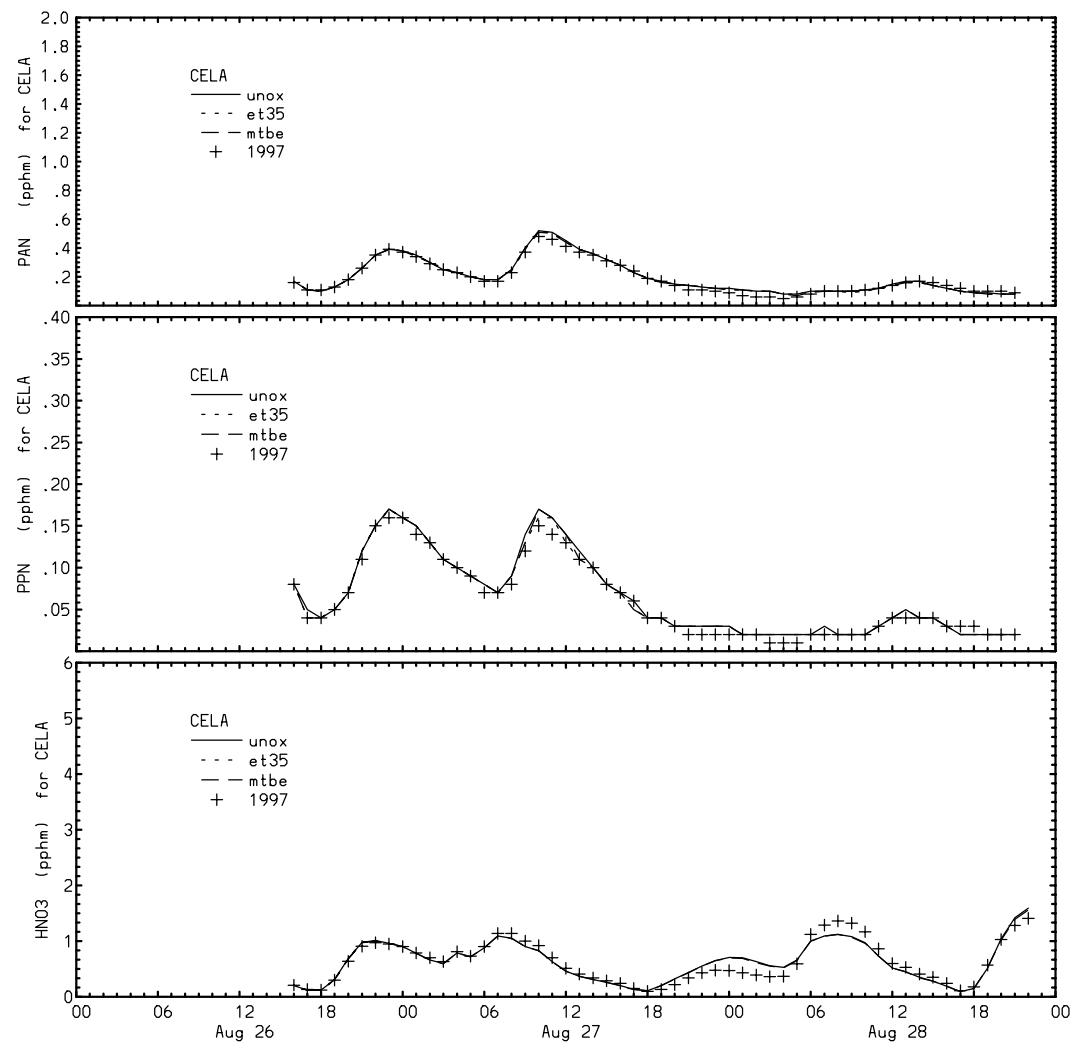


Figure 14. Time Series for PAN, PPN and HNO<sub>3</sub> at Los Angeles for 1997 and 2003 Scenarios

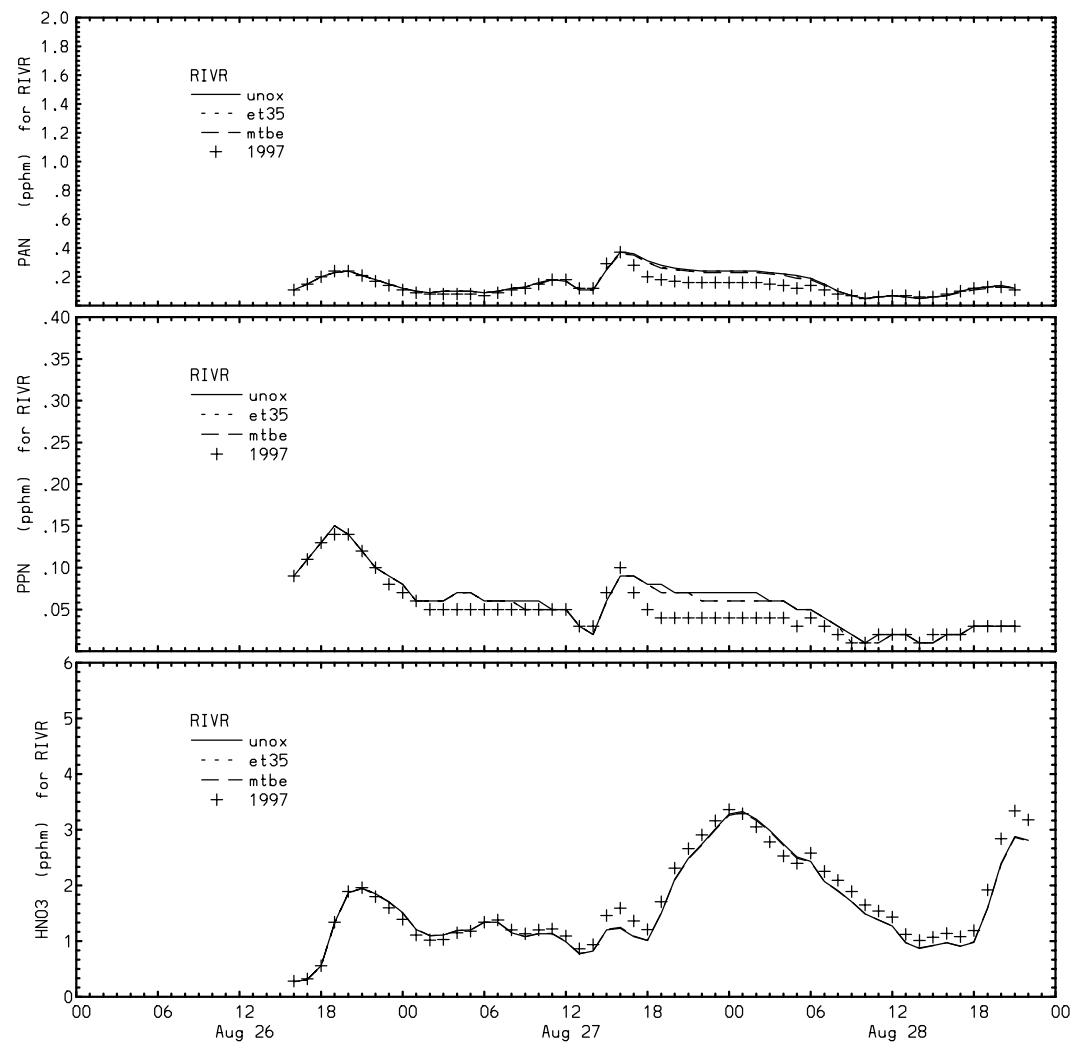


Figure 15. Time Series for PAN, PPN and HNO<sub>3</sub> at Riverside for 1997 and 2003 Scenarios

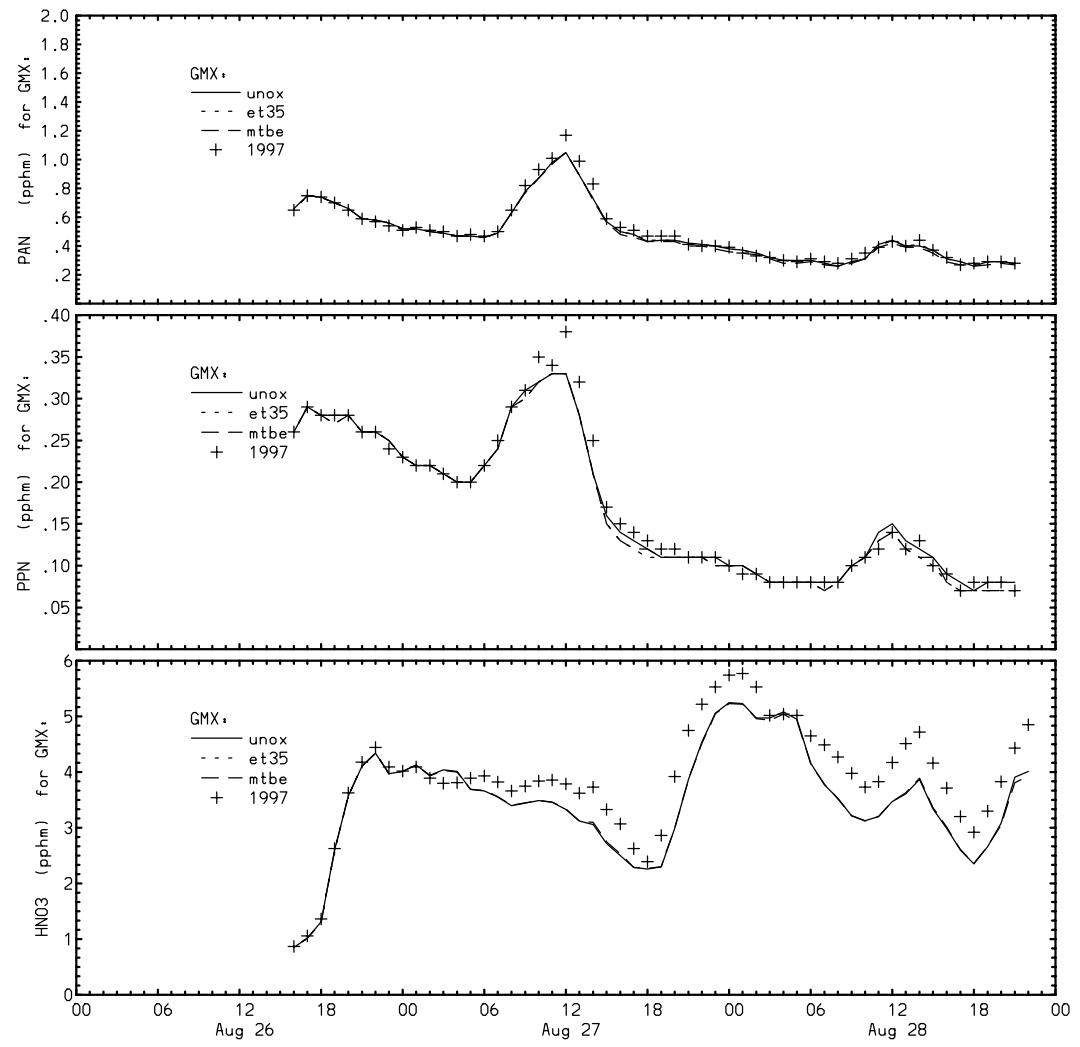


Figure 16. Time Series for PAN, PPN and HNO<sub>3</sub> at domain peak for 1997 and 2003 Scenarios

Table 9 shows maximum 24-hour average concentrations in the domain for selected pollutants. As shown, the 24-hr average ozone concentration decreases by less than 4% from 1997 to 2003. CO is reduced by up to 28% for the et35 and et35h scenarios. Similarly, the 24-hr benzene concentration is reduced by almost 36% between 1997 and 2003. The 24-hr average formaldehyde is reduced by 13%, but the 24-hr average acetaldehyde is unchanged. 24-hr nitric acid concentration is seen to decrease by 12% from 1997 to 2003, while PPN is essentially unchanged. The impact on 24-hr PAN concentration is also modest, with a decrease of up to 3% for the 2003/mtbe scenario.

**Table 9**  
**Domain 24-hr Average Concentrations**  
**For Each Scenario Considered**

<i>Simulation</i>	Domain 24-hr concentration (ppb)							
	<i>O3</i>	<i>CO</i>	<i>Formaldehyde</i> <sup>6</sup>	<i>Acetaldehyde</i> <sup>6</sup>	<i>C6H6</i>	<i>PAN</i>	<i>PPN</i>	<i>HNO3</i>
<b>1997</b>	148.0	1614	11.34	6.2	1.71	2.12	0.58	36.73
<b>2003</b>								
Et20 <sup>1</sup>	143.5	1252	9.85	6.2	1.15	2.12	0.60	32.43
Et35 <sup>2</sup>	142.7	1149	9.88	6.2	1.18	2.11	0.57	32.30
Mtbe <sup>3</sup>	142.9	1252	9.93	6.2	1.17	2.05	0.58	32.44
Unox <sup>4</sup>	143.9	1286	9.85	6.2	1.15	2.13	0.61	32.48
Et20h <sup>5</sup>	143.1	1252	9.76	6.2	1.10	2.06	0.60	32.36
Et35h <sup>5</sup>	142.4	1149	9.79	6.2	1.10	2.06	0.57	32.24

1 et20 = ethanol-based fully complying fuel (with oxygen content of 2.0%)

2 et35 = ethanol-based fully complying fuel (with oxygen content of 3.5%)

3 mtbe = current MTBE-based cleaner burning gasoline

4 unox = non-oxygenated fully complying fuel

5 Harley sensitivity runs (labeled h) differ from et20 and et35 in that Harley's headspace calculations derived fuel profile was used for hot soaks and running evaps.

6 formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation

## 12. Sensitivity Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. A large increase in hydrocarbon emissions will be expected to change the NOx-to-hydrocarbon ratio and significantly impact the radical flux. The sensitivity simulations considered for this study are listed in Table 10. To test the sensitivity of the model to a large increase in emissions, the motor vehicle hydrocarbon and CO emissions were increased by a factor of 3. However, for the et35hCO scenario the hydrocarbon emissions were increased by a factor of 3, and the CO emissions were increased to the same levels as the Unox scenario. The predicted domain peak concentrations from the sensitivity simulations are given in Table 11.

**Table 10**  
**Sensitivity Scenarios**

Scenario	Description
Sens/1997	Increased motor vehicle CO and ROG by factor of 3
Sens/2003/Et35h	Increased motor vehicle CO and ROG by factor of 3 for the Et35h fuel
Sens/2003/Et35hCO	Increased motor vehicle ROG by factor of 3 for the Et35h fuel, but CO levels same as for 2003/unox scenario

**Table 11**  
**Domain Hourly Peak Concentrations  
Using Emissions for Each Scenario Considered**

Sensitivity Simulation	Domain Peak (ppb)							
	O3	CO	Formaldehyde <sup>2</sup>	Acetaldehyde <sup>2</sup>	C6H6	PAN	PPN	HNO3
<b>Sens/1997<sup>1</sup></b>	422.1	7447.6	37.3	19.2	9.1	18.0	5.5	70.0
<b>Sens/2003</b>								
Et35h <sup>1</sup>	318.2	4347.7	25.4	14.6	4.7	11.7	3.5	54.1
Unox <sup>1</sup>	340.8	5193.1	25.7	14.0	5.4	12.1	3.7	54.4
Et35hCO <sup>1</sup>	325.5	5292.6	25.4	14.6	4.7	11.6	3.4	54.3

1. Sensitivity simulations have Motor Vehicle ROG\*3 and CO\*3 (except for Et35hCO which has same CO emissions as Unox)
2. formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation

Comparing Table 9 and Table 11, it is clear that predicted species concentrations increased significantly when the motor vehicle hydrocarbon and CO emissions were increased by a factor of 3. As expected, the 1997 scenario shows a larger increase in peak concentrations than the 2003 scenarios. This effect is due to the larger motor vehicle emissions in 1997. For example, peak ozone increases by a factor of 1.79 in 1997, whereas it only increases by a factor of 1.44 in 2003/et35h. Acetaldehyde increases by a factor of almost 2 in 1997 compared to 1.64 in 2003/et35h.

The Sens/2003/Et35hCO was created by increasing the motor vehicle hydrocarbon emissions by a factor of 3, but keeping the CO emissions at the Sens/2003/Unox levels. This is equivalent to an increase in CO and hydrocarbon emissions in the Sens/2003/Et35h (this is because the oxygenated fuels produce less CO emissions than non-oxygenated fuels). From Table 11, the predicted CO peak concentration in the 2003/Unox and 2003/Et35hCO are similar, as expected. However, the increase in CO emissions causes the predicted ozone to be slightly higher in the Et35hCO scenario compared to the Et35h simulation. The Et25hCO simulation shows that the difference in CO emissions between the Et35h and the Unox scenarios account for about 1/3 of the peak ozone increase.

### 13. Model Performance

A performance evaluation is the process of establishing that the air quality model is adequately reproducing the chemical and physical processes that generate smog. One aspect of model performance includes the sensitivity simulations described in the previous section. In this section we test the model's

ability to reproduce measured air quality data. For this purpose, an area and point emission inventory was prepared for a 1987 baseline simulation. Differences and ratios of observed and simulated peak concentrations were calculated for each day of the August 26-28, 1987 episode in the SCAQS domain.

Several statistical measures were used (ARB, 1992), including the Mean Absolute Gross Error (MAGE)

$$MAGE = \sum \frac{|C_s - C_o|}{N}$$

Where N is the number of observations,  $C_s$  is the simulated concentration and  $C_o$  is the observed concentration; Mean Absolute Normalized Gross Error (MANGE)

$$MANGE = \frac{1}{N} \sum \frac{|C_s - C_o|}{C_o};$$

Mean Bias (MBIAS):

$$MBIAS = \sum \frac{C_s - C_o}{N};$$

Normalized Mean Bias (NBIAS):

$$NBIAS = \frac{1}{N} \sum \frac{C_s - C_o}{C_o}$$

and the Unpaired Peak Estimation Accuracy (UPEA)

$$UPEA = \frac{C_s^{\max} - C_o^{\max}}{C_o^{\max}}$$

Where  $C_s^{\max}$  is the maximum estimated 1-hr concentration at any site in the domain, and  $C_o^{\max}$  is the maximum observed 1-hr concentration at any site in the domain.

The average statistics for all sites in the domain are given in Table 12 August 28, 1987. The UAM-FCM SAPRC97 tends to overpredict peak ozone only 4%. Peak NO<sub>2</sub> is within 10 percent of observed domain peak, but the model significantly under predicts peak CO and NO.

**Table 12**  
**UAM-FCM with SAPRC97**  
**Model Performance Evaluation**  
**(SCAQS Domain)**

	O3	CO	NO	NO2
Peak Ratio	1.04	0.79	0.44	1.07
MBIAS (pphm)	2.8	-14.2	-4.9	-1.4
MAGE (pphm)	3.8	77.1	5.1	3.1
NBIAS	0.32	0.07	0.71	-0.14
MANGE	0.38	0.48	0.76	0.60
UPEA	0.29	-0.08	0.09	0.37

Although the UAM has been widely applied to a number of episodes (see for example, Morris and Meyers, 1990), the UAM-FCM, on the other hand, has limited application since its development in 1995. Therefore it was considered appropriate to examine the model performance of the UAM-FCM when using a different chemical mechanism, such as the Carbon-Bond IV(CB-IV).

The CB-IV chemical mechanism uses the lumped structure approach to represent the atmospheric oxidation of hydrocarbons in ambient air (Gery *et al.*, 1989). Carbon-bond surrogates are used to represent the chemistry of the three most common type of carbon bonds (single: PAR, double: OLE, and the CHO-group: ALD2), and two molecular surrogates represent the chemistry of aromatic compounds (monoalkylbenzenes: TOL -based on toluene, di-and trialkylbenzenes: XYL -based on m-xylene). Ethene, isoprene, ethanol, methanol, formaldehyde, methylgioxal, gioxal, PAN are treated explicitly.

Carbon-Bond IV (version 6.21) was implemented into the UAM-FCM. We prepared area and point source emissions files, together with initial and boundary conditions for the August 26-28,1987 episode using speciation appropriate for the CB-IV mechanism. Table 13 summarizes the performance of the UAM-FCM with CBIV. Compared to the performance of the SAPRC97 mechanism in Tables 13, CB-IV tends to under predict peak ozone concentration 11% on the last day of the episode. However, both SAPRC97 and CB-IV have similar average performance for CO, NO and NO2. Overall, the UAM-FCM has similar model performance with either SAPRC97 or CB-IV. Figures 17 to 21 show a comparison of ozone, NO and NO2, as predicted by SAPRC97 and CB-IV, for Anaheim, Burbank, Downtown Los Angeles, Riverside and for the maximum concentration in the domain.

**Table 13**  
**UAM-FCM with CB4**  
**Model Performance Evaluation**  
**(SCAQS Domain)**

	O3	CO	NO	NO2
Peak Ratio	0.89	0.77	0.58	1.00
MBIAS (pphm)	-0.10	-25.1	-3.8	-1.3
MAGE (pphm)	2.70	77.1	4.5	2.8
NBIAS	0.05	0.00	-0.49	-0.12
MANGE	0.24	0.46	0.67	0.56
UPEA	0.04	-0.02	0.83	0.30



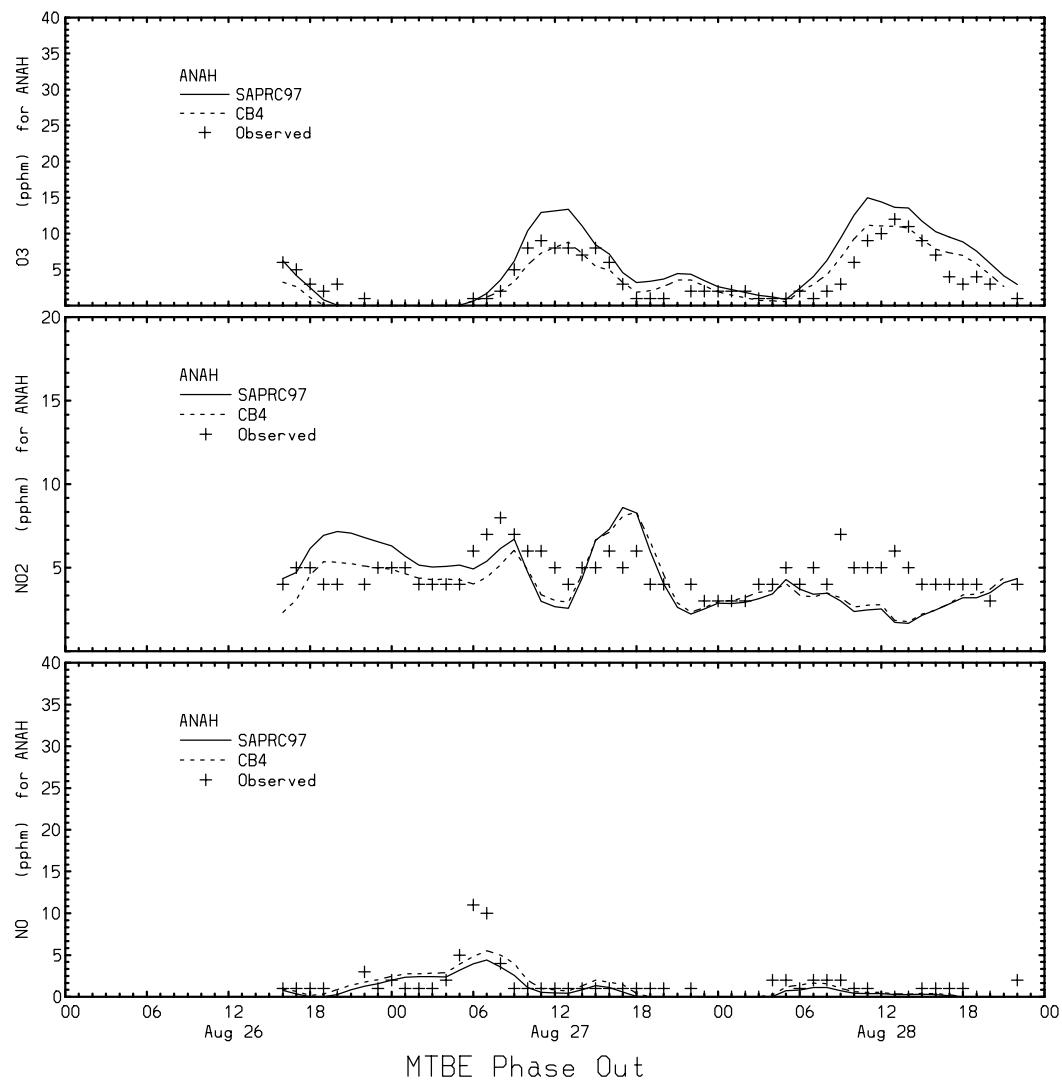


Figure 17. Comparison of Predicted Ozone, NO and NO<sub>2</sub> by SAPRC97 and CB-IV against ambient data at Anaheim (SCAQS 1987)

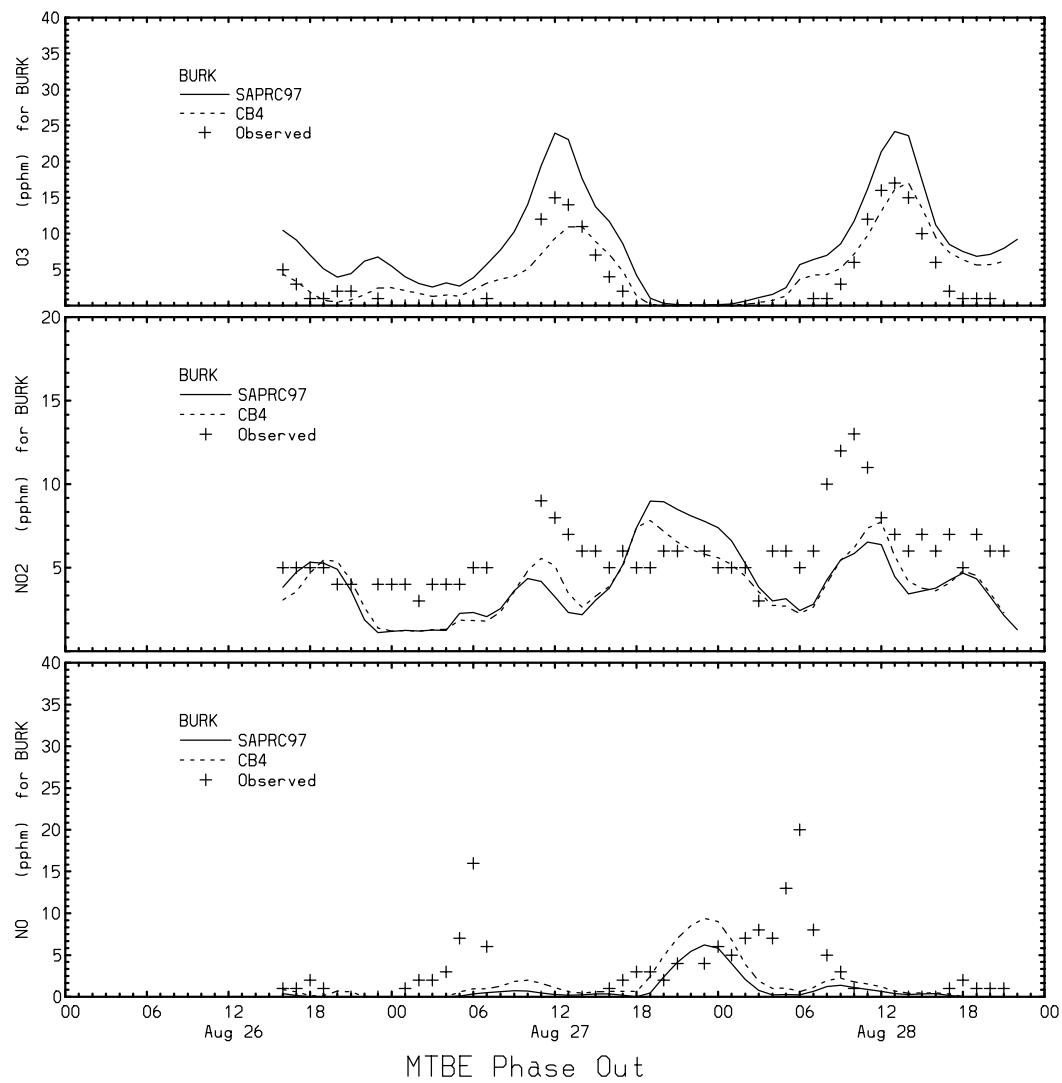


Figure 18. Comparison of Predicted Ozone, NO and NO<sub>2</sub> by SAPRC97 and CB-IV against ambient data at Burbank (SCAQS 1987)

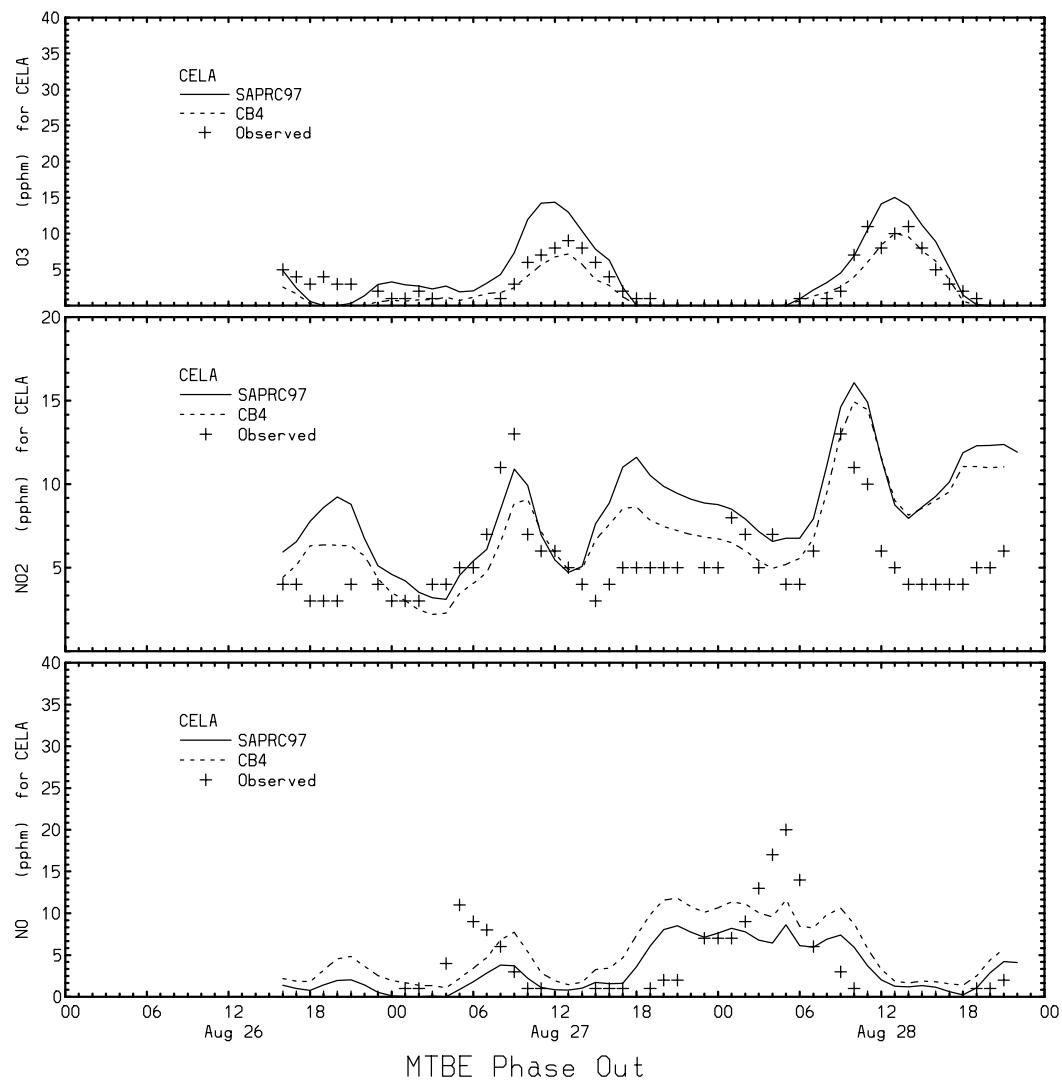


Figure 19. Comparison of Predicted Ozone, NO and NO<sub>2</sub> by SAPRC97 and CB-IV against ambient data at Los Angeles (SCAQs 1987)

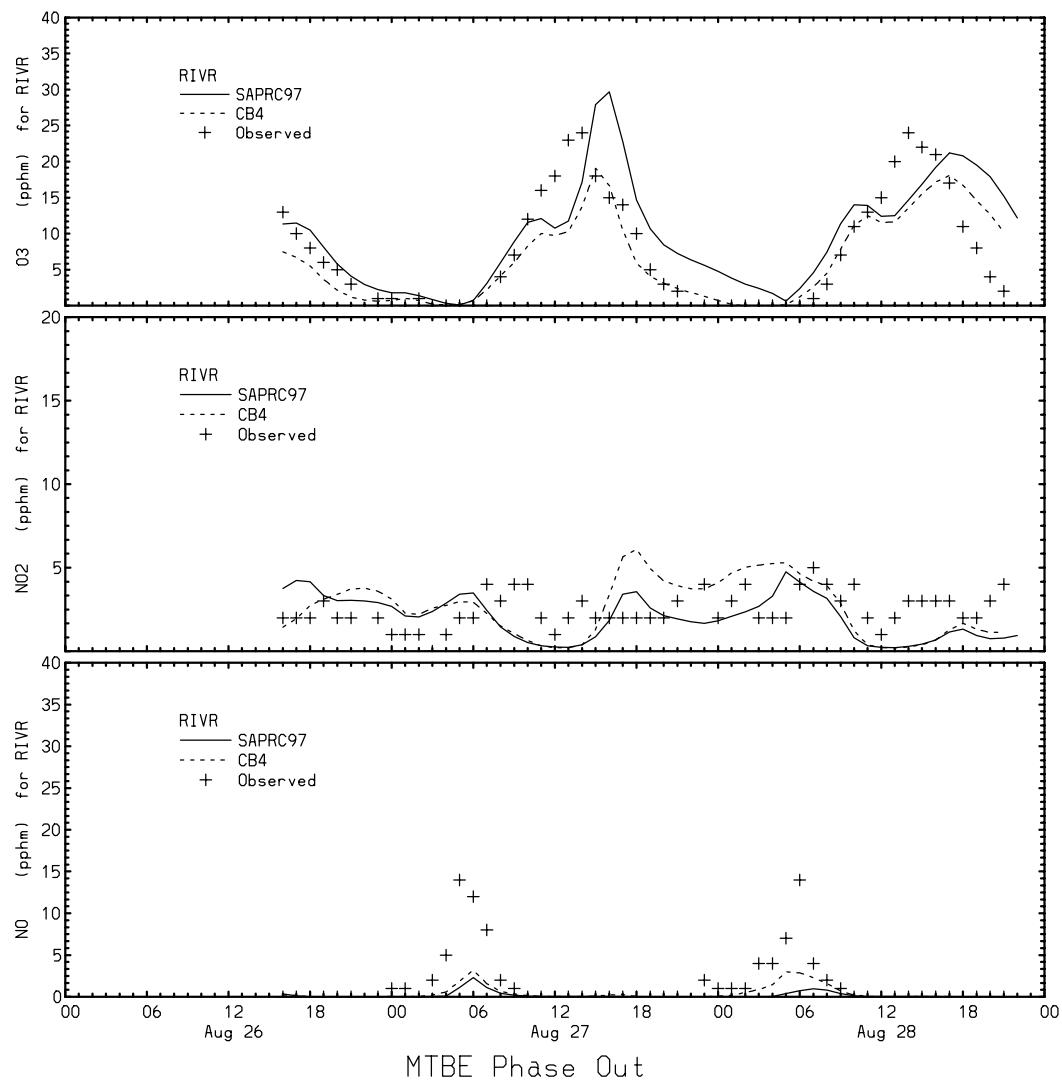


Figure 20. Comparison of Predicted Ozone, NO and NO<sub>2</sub> by SAPRC97 and CB-IV against ambient data at Riverside (SCAQs 1987)

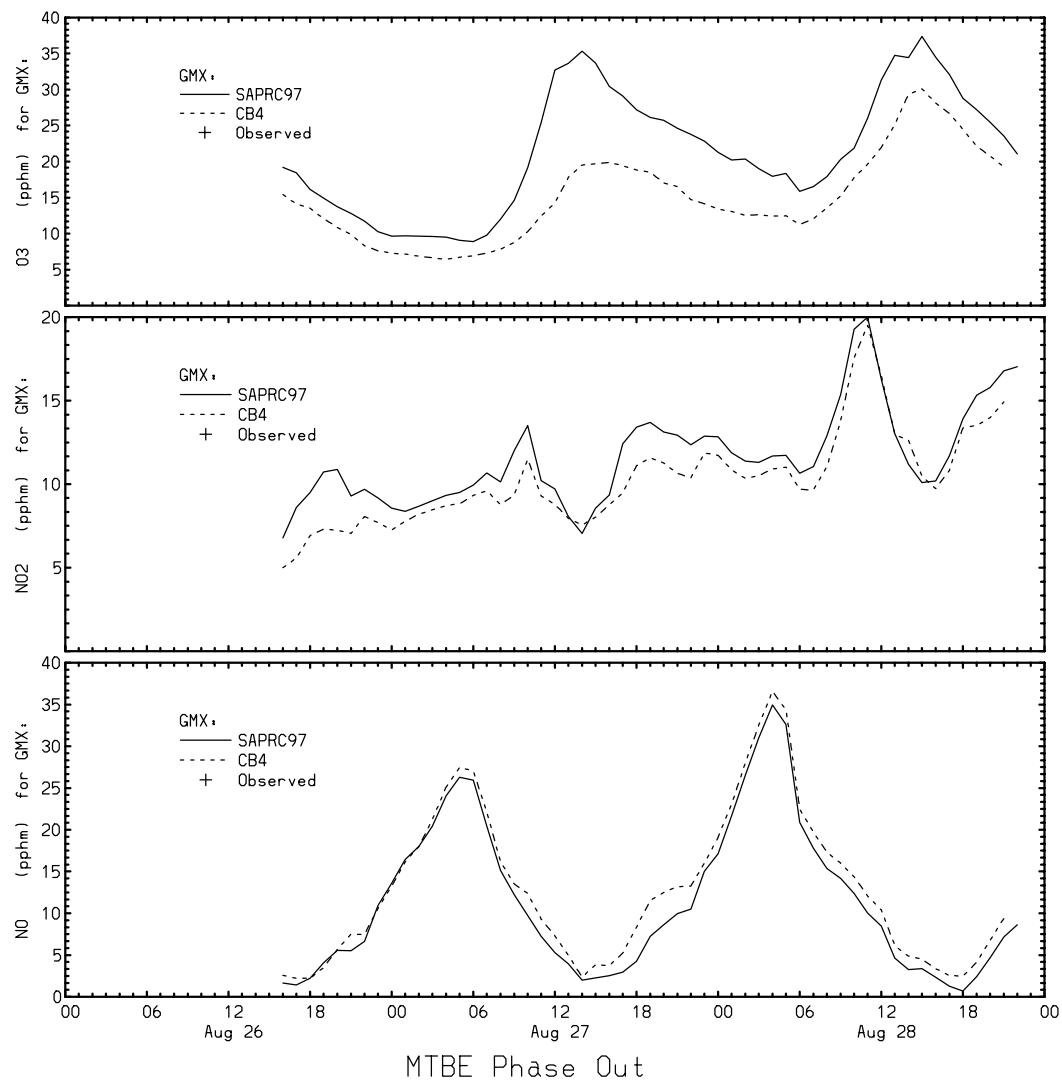


Figure 21. Comparison of Predicted Ozone, NO and NO<sub>2</sub> by SAPRC97 and CB-IV against ambient data at the Domain maximum (SCAQS 1987)

## 14. Exposure

Domain Population Exposure to pollutant k ( $P_k$ ) was defined as a 24-hr average

$$P_k = \sum_{ij} \sum_{t=0}^{t=23} C_{ij}^k(t) * p_{ij} * \frac{1}{24}$$

Where  $C_{ij}^k(t)$  is the simulated hourly concentration of pollutant k at cell (i,j) of the domain and starting time t, and  $p_{ij}$  is the population in cell (i,j). Population data was obtained from the Department of Finance (1993) and extrapolated from the 1990 baseline year to 1997 and 2003 using factors provided by the Department of Finance. The population data was further gridded for each year of interest. The population exposure was calculated using the results of the last simulated day of the episode. Table 14 shows 24-hr average population exposure for ozone and carbon monoxide (CO).

**Table 14**  
**Domain 24-hr average Population Exposure**  
**To Ozone and CO on August 28, 1987**  
**(ppm\*person/1000)**

Scenario	Ozone Exposure	Carbon Monoxide Exposure
1997	1,061.2	15,662.8
2003/Mtbe	1,250.8	14,198.7
2003/Et20	1,257.9	14,201.8
2003/Et20h	1,251.7	14,200.8
2003/Et35	1,249.2	13,204.2
2003/Et35h	1245.0	13,203.2
2003/Unox	1,263.1	14,533.4

2003 ozone exposure increases up to 18.5% for the oxygenated fuels over the base year, and 19% for the Unox scenario. CO exposure decreases almost 9% for the oxygenated fuels, and 7% for the Unox scenario . The increase in ozone exposure is probably due to increased population. From Table 9a, the 24-hr ozone concentration is expected to decrease by about 4% from 1997 to 2003. However, the total population in the domain is estimated to increase from 16,926,408 in 1997 to 18,703,580 (i.e., about a 10% increase) in 2003. The decrease in CO is consistent with the expected decrease in CO emissions from 1997 to 2003, tempered by an increase in population.

## 15. Model Use

It is important to bear in mind that the model results for this study are being used in a relative, rather than absolute sense. That is, the model was used to estimate the change from 1997 MTBE gasoline to ethanol-containing and non-oxygenated gasolines in 2003, rather than predict absolute values in 2003. The estimated changes were then used to adjust the base base year measurements to future values. The modeling community is in general agreement that models are best used in a relative sense.

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## **Attachment A. SAPRC97 Photochemical Reaction Mechanism**

This Attachment includes a listing of the SAPRC97 mechanism. A separate listing is provided for the isoprene reaction mechanism and for other species treated explicitly. The SAPRC mechanism used in the study described in this report included all the reactions listed in this Attachment. Interpretation of reactions rates constants can be found in Kumar et a. (1996).

### A.1 SAPRC97

1) PF=NO2 ;NO2 + HV = NO + O  
 2) 6.0E-34, 0.0, -2.3 ;O + O2 + M = O3 + M  
 3A) 6.5E-12, -0.238 ;O + NO2 = NO + O2  
 !  
 3B) FALLOFF ;O + NO2 = NO3 + M  
 9.0E-32 0.0 -2.0  
 2.2E-11 0.0 0.0  
 0.6 1.0  
 !  
 4) 2.00E-12, 2.782 ;O3 + NO = NO2 + O2  
 5) 1.400E-13, 4.968 ;O3 + NO2 = O2 + NO3  
 6) 1.7E-11, -0.298 ;NO + NO3 = #2 NO2  
 7) 3.300E-39, -1.05 ;NO + NO + O2 = #2 NO2  
 !  
 8) FALLOFF ;NO2 + NO3 = N2O5  
 2.2E-30 0.0 -4.3  
 1.5E-12 0.0 -0.5  
 0.6 1.0  
 !  
 9) 9.09E+26, 22.26 ;N2O5 + #RCON8 = NO2 + NO3  
 10) 1.0E-21 0.0 ;N2O5 + H2O = #2 HNO3  
 11) 2.5E-14, 2.44 ;NO2 + NO3 = NO + NO2 + O2  
 12A) PF=NO3NO ;NO3 + HV = NO + O2  
 12B) PF=NO3NO2 ;NO3 + HV = NO2 + O  
 13A) PF=O3O3P ;O3 + HV = O + O2  
 13B) PF=O3O1D ;O3 + HV = O\*1D2 + O2  
 14) 2.2E-10, 0.0 ;O\*1D2 + H2O = #2 HO  
 15) 1.919E-11, -0.251 ;O\*1D2 + M = O + M  
 !  
 16) FALLOFF ;HO + NO = HONO  
 7.0E-31 0.0 -2.6  
 1.5E-11 0.0 -0.5  
 0.6 1.0  
 !  
 17) PF=HONO ;HONO + HV = HO + NO  
 !  
 18) FALLOFF ;HO + NO2 = HNO3  
 2.6E-30 0.0 -3.2  
 2.4E-11 0.0 -1.3  
 0.6 1.0  
 !  
 19) 6.45E-15, -1.652 ;HO + HNO3 = H2O + NO3 ! 1 ATM ONLY.  
 21) 2.4E-13, 0.0 ;HO + CO = HO2 + CO2 !1 ATM ONLY  
 22) 1.600E-12, 1.87 ;HO + O3 = HO2 + O2  
 23) 3.700E-12, -0.48 ;HO2 + NO = HO + NO2  
 !  
 24) FALLOFF ;HO2 + NO2 = HNO4  
 1.8E-31 0.0 -3.2  
 4.7E-12 0.0 -1.4  
 0.6 1.0  
 !  
 25) 4.76E+26, 21.66 ;HNO4 + #RCON24 = HO2 + NO2  
 27) 1.3E-12, -0.755 ;HNO4 + HO = H2O + NO2 + O2

28) 1.100E-14, 0.994 ;HO<sub>2</sub> + O<sub>3</sub> = HO + #2 O<sub>2</sub>  
 29A) 2.2E-13, -1.23 ;HO<sub>2</sub> + HO<sub>2</sub> = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>  
 29B) 1.9E-33, -1.95 ;HO<sub>2</sub> + HO<sub>2</sub> + M = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>  
 29C) 3.1E-34, -5.60 ;HO<sub>2</sub> + HO<sub>2</sub> + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 !29D) 2.7E-54, -6.32 ;HO<sub>2</sub> + HO<sub>2</sub> + M + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 29D) 6.6E-35, -6.32 ;HO<sub>2</sub> + HO<sub>2</sub> + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O !(1 ATM ONLY)  
 30A) 2.2E-13, -1.23 ;NO<sub>3</sub> + HO<sub>2</sub> = HNO<sub>3</sub> + O<sub>2</sub>  
 30B) 1.9E-33, -1.95 ;NO<sub>3</sub> + HO<sub>2</sub> + M = HNO<sub>3</sub> + O<sub>2</sub>  
 30C) 3.1E-34, -5.60 ;NO<sub>3</sub> + HO<sub>2</sub> + H<sub>2</sub>O = HNO<sub>3</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 30D) 6.6E-35, -6.32 ;NO<sub>3</sub> + HO<sub>2</sub> + H<sub>2</sub>O = HNO<sub>3</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 31) PF=H<sub>2</sub>O<sub>2</sub> ;H<sub>2</sub>O<sub>2</sub> + HV = #2 HO  
 32) 3.300E-12, 0.397 ;H<sub>2</sub>O<sub>2</sub> + HO = HO<sub>2</sub> + H<sub>2</sub>O  
 33) 4.60E-11, -0.457 ;HO + HO<sub>2</sub> = H<sub>2</sub>O + O<sub>2</sub>  
 B1) 4.200E-12, -0.360 ;RO<sub>2</sub> + NO = NO  
 !  
 B2) FALLOFF ;RCO<sub>3</sub> + NO = NO  
 5.65E-28 0.0 -7.1  
 2.64E-11 0.0 -0.9  
 0.27 1.0  
 !  
 B4) FALLOFF ;RCO<sub>3</sub> + NO<sub>2</sub> = NO<sub>2</sub>  
 2.57E-28 0.0 -7.1  
 12.0E-12 0.0 -0.9  
 0.30 1.0  
 !  
 B5) 3.40E-13, -1.590 ;RO<sub>2</sub> + HO<sub>2</sub> = HO<sub>2</sub>  
 B6) 3.40E-13, -1.590 ;RCO<sub>3</sub> + HO<sub>2</sub> = HO<sub>2</sub>  
 B8) 1.0E-15 ;RO<sub>2</sub> + RO<sub>2</sub> =  
 B9) 1.86E-12, -1.053 ;RO<sub>2</sub> + RCO<sub>3</sub> =  
 B10) 2.8E-12, -1.053 ;RCO<sub>3</sub> + RCO<sub>3</sub> =  
 B11) SAMEK B1 ;RO<sub>2</sub>-R + NO = NO<sub>2</sub> + HO<sub>2</sub>  
 B12) SAMEK B5 ;RO<sub>2</sub>-R + HO<sub>2</sub> = XOOH  
 B13) SAMEK B8 ;RO<sub>2</sub>-R + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub>  
 B14) SAMEK B9 ;RO<sub>2</sub>-R + RCO<sub>3</sub> = RCO<sub>3</sub> + #.5 HO<sub>2</sub>  
 B19) SAMEK B1 ;RO<sub>2</sub>-N + NO = RNO<sub>3</sub>  
 B20) SAMEK B5 ;RO<sub>2</sub>-N + HO<sub>2</sub> = XOOH + MEK + #1.5 XC  
 B21) SAMEK B8 ;RO<sub>2</sub>-N + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub> + MEK + #1.5 XC  
 B22) SAMEK B9 ;RO<sub>2</sub>-N + RCO<sub>3</sub> = RCO<sub>3</sub> + #.5 HO<sub>2</sub> + MEK + #1.5 XC  
 B15) SAMEK B1 ;R<sub>2</sub>O<sub>2</sub> + NO = NO<sub>2</sub>  
 B16) SAMEK B5 ;R<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub> =  
 B17) SAMEK B8 ;R<sub>2</sub>O<sub>2</sub> + RO<sub>2</sub> = RO<sub>2</sub>  
 B18) SAMEK B9 ;R<sub>2</sub>O<sub>2</sub> + RCO<sub>3</sub> = RCO<sub>3</sub>  
 B23) SAMEK B1 ;RO<sub>2</sub>-XN + NO = XN  
 B24) SAMEK B5 ;RO<sub>2</sub>-XN + HO<sub>2</sub> = XOOH  
 B25) SAMEK B8 ;RO<sub>2</sub>-XN + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub>  
 B26) SAMEK B9 ;RO<sub>2</sub>-XN + RCO<sub>3</sub> = RCO<sub>3</sub> + HO<sub>2</sub>  
 G2) SAMEK B1 ;RO<sub>2</sub>-NP + NO = NPHE  
 G3) SAMEK B5 ;RO<sub>2</sub>-NP + HO<sub>2</sub> = XOOH + #6 XC  
 G4) SAMEK B8 ;RO<sub>2</sub>-NP + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub> + #6 XC  
 G5) SAMEK B9 ;RO<sub>2</sub>-NP + RCO<sub>3</sub> = RCO<sub>3</sub> + HO<sub>2</sub> + #6 XC  
 B7) PF=CO<sub>2</sub>H ;XOOH + HV = HO<sub>2</sub> + HO  
 B7A) 1.18E-12, -0.254 ;HO + XOOH = HO  
 B7B) 1.79E-12, -0.435 ;HO + XOOH = RO<sub>2</sub>-R + RO<sub>2</sub>  
 C1) PF=HCHONEWR ;HCHO + HV = #2 HO<sub>2</sub> + CO  
 C2) PF=HCHONEWM ;HCHO + HV = H<sub>2</sub> + CO  
 C3) 1.125E-12 -1.288 2.0 ;HCHO + HO = HO<sub>2</sub> + CO + H<sub>2</sub>O

C4) 9.7E-15, -1.242  
 C4A) 2.4E+12, 13.91  
 C4B) SAMEK B1  
 C9) 2.8E-12, 5.00  
 C10) 5.55E-12, -0.618  
 C11A) PF=CCHOR  
 C12) 1.4E-12, 3.696  
 C25) 8.5E-12 -0.50  
 C26) PF=RCHO  
 C27) 1.4E-12, 3.696  
 C38) 4.81E-13 0.457 2.0  
 C39) PF=ACET-93C  
 C44) 2.92E-13 -0.823 2.0  
  
 C57) PF=KETONE  
  
 C95) 2.191E-11, 1.408  
  
 C13) SAMEK B2  
 C14) SAMEK B4  
 C15) SAMEK B6  
 C16) SAMEK B9  
 C17) SAMEK B10  
 !  
 C18) FALLOFF  
 4.90E-03 23.972 0.0  
 4.00E+16 27.079 0.0  
 0.30 1.00  
 !  
 C28) SAMEK B2  
 C29) 8.4E-12 0.0 0.0  
 C30) SAMEK B6  
 C31) SAMEK B9  
 C32) SAMEK B10  
 C33) 1.6E+17, 27.966  
 TBON) 2.4E-11  
 TBOD) 7.5E+14, 16.2  
 C58A) PF=GLYOXAL1  
 C58B) PF=GLYOXAL2  
 C59) 1.14E-11  
  
 C60) SAMEK C12  
  
 C62) SAMEK B2  
 C63) SAMEK B4  
 C64) SAMEK C18  
 C65) SAMEK B6  
 C66) SAMEK B9  
 C67) SAMEK B10  
 C68A) PF=MEGLYOX1  
 C68B) PF=MEGLYOX2  
 C69) 1.72E-11  
 C70) SAMEK C12  
 G46) 2.63E-11  
  
 G51) 3.6E-12

;HCHO + HO2 = HOCOO  
 ;HOCOO = HO2 + HCHO  
 ;HOCOO + NO = XC + NO2 + HO2  
 ;HCHO + NO3 = HNO3 + HO2 + CO  
 ;CCHO + HO = CCO-O2 + H2O + RCO3  
 ;CCHO + HV = CO + HO2 + HCHO + RO2-R + RO2  
 ;CCHO + NO3 = HNO3 + CCO-O2 + RCO3  
 ;RCHO + HO = C2CO-O2 + RCO3  
 ;RCHO + HV = CCHO + RO2-R + RO2 + CO + HO2  
 ;NO3 + RCHO = HNO3 + C2CO-O2 + RCO3  
 ;ACET + HO = R2O2 + HCHO + CCO-O2 + RCO3 + RO2  
 ;ACET + HV = CCO-O2 + HCHO + RO2-R + RCO3 + RO2  
 ;MEK + HO = H2O + #.5 "CCHO + HCHO + CCO-O2 + &  
 C2CO-O2 " + RCO3 + #1.5 "R2O2 + RO2 "  
 ;MEK + HV + #0.1 = CCO-O2 + CCHO + RO2-R + RCO3 &  
 + RO2  
 ;RNO3 + HO = NO2 + #.155 MEK + #1.05 RCHO + &  
 #.48 CCHO + #.16 HCHO + #.11 XC + #1.39 "R2O2 + RO2 "  
 ;CCO-O2 + NO = CO2 + NO2 + HCHO + RO2-R + RO2  
 ;CCO-O2 + NO2 = PAN  
 ;CCO-O2 + HO2 = XOOH + CO2 + HCHO  
 ;CCO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + HCHO  
 ;CCO-O2 + RCO3 = RCO3 + HO2 + CO2 + HCHO  
  
 ;PAN = CCO-O2 + NO2 + RCO3

;C2CO-O2 + NO = CCHO + RO2-R + CO2 + NO2 + RO2  
 ;C2CO-O2 + NO2 = PPN  
 ;C2CO-O2 + HO2 = XOOH + CCHO + CO2  
 ;C2CO-O2 + RO2 = RO2 + #.5 HO2 + CCHO + CO2  
 ;C2CO-O2 + RCO3 = RCO3 + HO2 + CCHO + CO2  
 ;PPN = C2CO-O2 + NO2 + RCO3  
 ;C2(C)-O + NO2 = RNO3 + #-2 XC  
 ;C2(C)-O = ACET + HCHO + RO2-R + RO2  
 ;GLY + HV = #.8 HO2 + #.45 HCHO + #1.55 CO  
 ;GLY + HV + #0.029 = #.13 HCHO + #1.87 CO  
 ;GLY + HO = #.6 HO2 + #1.2 CO + #.4 "HCOCO-O2 + &  
 RCO3 "  
 ;GLY + NO3 = HNO3 + #.6 HO2 + #1.2 CO + &  
 #.4 "HCOCO-O2 + RCO3 "  
 ;HCOCO-O2 + NO = NO2 + CO2 + CO + HO2  
 ;HCOCO-O2 + NO2 = GPAN  
 ;GPAN = HCOCO-O2 + NO2 + RCO3  
 ;HCOCO-O2 + HO2 = XOOH + CO2 + CO  
 ;HCOCO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + CO  
 ;HCOCO-O2 + RCO3 = RCO3 + HO2 + CO2 + CO  
 ;MGLY + HV = HO2 + CO + CCO-O2 + RCO3  
 ;MGLY + HV + #.107 = HO2 + CO + CCO-O2 + RCO3  
 ;MGLY + HO = CO + CCO-O2 + RCO3  
 ;MGLY + NO3 = HNO3 + CO + CCO-O2 + RCO3  
 ;HO + PHEN = #.15 RO2-NP + #.85 RO2-R + #.2 GLY + &  
 #4.7 XC + RO2  
 ;NO3 + PHEN = HNO3 + BZ-O

G52)	4.2E-11	;HO + CRES = #.15 RO2-NP + #.85 RO2-R + #.2 MGLY + & #5.5 XC + RO2
G57)	2.1E-11	;NO3 + CRES = HNO3 + BZ-O + XC
G30)	1.29E-11	;BALD + HO = BZ-CO-O2 + RCO3
G31)	PF=BZCHO	;BALD + HV + #.05 = #7 XC
G32)	1.4E-12, 3.747	;BALD + NO3 = HNO3 + BZ-CO-O2
G33)	SAMEK B2	;BZ-CO-O2 + NO = BZ-O + CO2 + NO2 + R2O2 + RO2
G34)	8.4E-12 0.0 0.0	;BZ-CO-O2 + NO2 = PBZN
G36)	SAMEK B6	;BZ-CO-O2 + HO2 = XOOH + CO2 + PHEN
G37)	SAMEK B9	;BZ-CO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + PHEN
G38)	SAMEK B10	;BZ-CO-O2 + RCO3 = RCO3 + HO2 + CO2 + PHEN
G35)	1.6E+15, 25.90	;PBZN = BZ-CO-O2 + NO2 + RCO3
G43)	1.3E-11, -0.596	;BZ-O + NO2 = NPHE
G44)	SAMEK B5	;BZ-O + HO2 = PHEN
G45)	1.0E-3	;BZ-O = PHEN
G58)	3.6E-12	;NPHE + NO3 = HNO3 + BZ(NO2)-O
G59)	SAMEK G43	;BZ(NO2)-O + NO2 = #2 XN + #6 XC ! DINITROPHENOL
G60)	SAMEK B5	;BZ(NO2)-O + HO2 = NPHE
G61)	SAMEK G45	;BZ(NO2)-O = NPHE
G7)	1.14E-11	;HO + AFG1 = HCOCO-O2 + RCO3
G8)	PF=ACROLEIN	;AFG1 + HV + #0.077 = HO2 + HCOCO-O2 + RCO3
U2OH)	1.72E-11	;HO + AFG2 = C2CO-O2 + RCO3
U2HV)	PF=ACROLEIN	;AFG2 + HV = HO2 + CO + CCO-O2 + RCO3
RCH4)	6.255E-13 2.548 2.0	;CH4 + HO = HCHO + RO2-R + RO2
RZ1)	1.0	;;(HCHO2) = #.7 HCOOH + #.12 "HO + HO2 + CO" + & #.18 "H2 + CO2"
RZ2)	1.0	;;(CCHO2) = #.25 CCOOH + #.15 "CH4 + CO2" + #.6 HO + & #.3 "CCO-O2 + RCO3" + #.3 "RO2-R + HCHO + CO + & RO2"
RZ3)	1.0	;;(RCHO2) = #.25 CCOOH + #.15 CO2 + #.6 HO + & #.3 "C2CO-O2 + RCO3" + #.3 "RO2-R + CCHO + CO + & RO2" + #.55 XC
RZ4)	1.0	;;(C(C)CO2) = HO + R2O2 + HCHO + CCO-O2 + RCO3 + RO2
RZ5)	1.0	;;(C(R)CO2) = HO + CCO-O2 + CCHO + R2O2 + RCO3 + RO2
RZ6)	1.0	;;(CYCCO2) = #.3 "HO + C2CO-O2 + R2O2 + RCO3 + & RO2" + #.3 RCHO + #4.2 XC
RZ7)	1.0	;;(BZCHO2) = #.5 "BZ-O + R2O2 + CO + HO"
ETOH)	1.960E-12 -0.870	;;ETHE + HO = RO2-R + RO2 + #1.56 HCHO + #.22 CCHO
ETO3)	9.140E-15 5.127	;;ETHE + O3 = HCHO + (HCHO2)
ETN3)	5.430E-12 6.043	;;ETHE + NO3 = R2O2 + RO2 + #2 HCHO + NO2
ETOA)	1.040E-11 1.574	;;ETHE + O = RO2-R + HO2 + RO2 + HCHO + CO
A1OH)		;HO + ALK1 = #A1OHRR RO2-R + #A1OHNR RO2-N + & #A1OHXN RO2-XN + #A1OHNP RO2-NP + #A1OHRH HO2 + & #A1OHR2 R2O2 + #A1OHR3 RO2 + #A1OHA1 HCHO + & #A1OHA2 CCHO + #A1OHA3 RCHO + #A1OKH3 ACET + & #A1OKH4 MEK + #A1OHC0 CO + #A1OHC2 CO2 + & #A1OPH PHEN + #A1OHCRCRES + #A1OHBZ BALD + & #A1OGL GLY + #A1OHCMLGLY + #A1OHU1 AFG1 + & #A1OHU2 AFG2 + #A1OHTB C2(C)-O + #A1OHQ1 CCO-O2 + & #A1OHQ2 C2CO-O2 + #A1OHQS RCO3 + #A1OHCXC XC
A2OH)		;HO + ALK2 = #A2OHRR RO2-R + #A2OHNR RO2-N + & #A2OHXN RO2-XN + #A2OHNP RO2-NP + #A2OHRH HO2 + & #A2OHR2 R2O2 + #A2OHR3 RO2 + #A2OHA1 HCHO + & #A2OHA2 CCHO + #A2OHA3 RCHO + #A2OKH3 ACET + &

!

#A2OHK4 MEK + #A2OHC0 CO + #A2OHC2 CO2 + &  
 #A2OHPH PHEN + #A2OHCRES + #A2OHBZ BALD + &  
 #A2OHGL GLY + #A2OHMG MGLY + #A2OHU1 AFG1 + &  
 #A2OHU2 AFG2 + #A2OHTB C2(C)-O + #A2OHQ1 CCO-O2 + &  
 #A2OHQ2 C2CO-O2 + #A2OHQS RCO3 + #A2OHXC XC  
 !  
 B1OH)  
 ;HO + ARO1 = #B1OHRR RO2-R + #B1OHNRO2-N + &  
 #B1OHXN RO2-XN + #B1OHNPR O2-NP + #B1OHRH HO2 + &  
 #B1OHR2 R2O2 + #B1OHRSS RO2 + #B1OHA1 HCHO + &  
 #B1OHA2 CCHO + #B1OHA3 RCHO + #B1OHK3 ACET + &  
 #B1OHK4 MEK + #B1OHC0 CO + #B1OHC2 CO2 + &  
 #B1OHPH PHEN + #B1OHCRES + #B1OHBZ BALD + &  
 #B1OHGL GLY + #B1OHMG MGLY + #B1OHU1 AFG1 + &  
 #B1OHU2 AFG2 + #B1OHTB C2(C)-O + #B1OHQ1 CCO-O2 + &  
 #B1OHQ2 C2CO-O2 + #B1OHQS RCO3 + #B1OHXC XC  
 !  
 B2OH)  
 ;HO + ARO2 = #B2OHRR RO2-R + #B2OHNRO2-N + &  
 #B2OHXN RO2-XN + #B2OHNPR O2-NP + #B2OHRH HO2 + &  
 #B2OHR2 R2O2 + #B2OHRSS RO2 + #B2OHA1 HCHO + &  
 #B2OHA2 CCHO + #B2OHA3 RCHO + #B2OHK3 ACET + &  
 #B2OHK4 MEK + #B2OHC0 CO + #B2OHC2 CO2 + &  
 #B2OHPH PHEN + #B2OHCRES + #B2OHBZ BALD + &  
 #B2OHGL GLY + #B2OHMG MGLY + #B2OHU1 AFG1 + &  
 #B2OHU2 AFG2 + #B2OHTB C2(C)-O + #B2OHQ1 CCO-O2 + &  
 #B2OHQ2 C2CO-O2 + #B2OHQS RCO3 + #B2OHXC XC  
 !  
 O1OH)  
 ;OLE1 + HO = #O1OHRR RO2-R + #O1OHRN RO2-N + &  
 #O1OHRSS RO2 + #O1OHA1 HCHO + #O1OHA2 CCHO + &  
 #O1OHA3 RCHO + #O1OHK3 ACET + #O1OHK4 MEK + &  
 #O1OHBZ BALD + #O1OHXC XC  
 !  
 O1O3)  
 ;OLE1 + O3 = #O1O3A1 HCHO + #O1O3A2 CCHO + &  
 #O1O3A3 RCHO + #O1O3K3 ACET + #O1O3K4 MEK + &  
 #O1O3BZ BALD + #O1O3Z1 (HCHO2) + #O1O3Z2 (CCHO2) + &  
 #O1O3Z3 (RCHO2) + #O1O3Z4 (C(C)CO2) + &  
 #O1O3Z5 (C(R)CO2) + #O1O3Z6 (CYCCO2) + &  
 #O1O3Z8 (BZCHO2) + #O1O3OH HO + #O1O3RR RO2-R + &  
 #O1O3RN RO2-N + #O1O3XN RO2-XN + #O1O3NP RO2-NP + &  
 #O1O3RH HO2 + #O1O3R2 R2O2 + #O1O3RS RO2 + &  
 #O1O3Q1 CCO-O2 + #O1O3Q2 C2CO-O2 + #O1O3QS RCO3 + &  
 #O1O3XC XC  
 !  
 O1OA)  
 ;OLE1 + O = #O1OARR RO2-R + #O1OARH HO2 + &  
 #O1OARS RO2 + #O1OAA1 HCHO + #O1OAA3 RCHO + &  
 #O1OAK4 MEK + #O1OACO CO + #O1OAXC XC  
 !  
 O1N3)  
 ;OLE1 + NO3 = #O1N3N2 NO2 + #O1N3N3 HNO3 + &  
 #O1N3RH HO2 + #O1N3RR RO2-R + #O1N3RN RO2-N + &  
 #O1N3R2 R2O2 + #O1N3RS RO2 + #O1N3A1 HCHO + &  
 #O1N3A2 CCHO + #O1N3A3 RCHO + #O1N3K3 ACET + &  
 #O1N3K4 MEK + #O1N3BZ BALD + #O1N3XC XC  
 !  
 O2OH)  
 ;OLE2 + HO = #O2OHRR RO2-R + #O2OHRN RO2-N + &  
 #O2OHRSS RO2 + #O2OHA1 HCHO + #O2OHA2 CCHO + &  
 #O2OHA3 RCHO + #O2OHK3 ACET + #O2OHK4 MEK + &  
 #O2OHBZ BALD + #O2OHXC XC

!

O2O3) ;OLE2 + O3 = #O2O3A1 HCHO + #O2O3A2 CCHO + &  
 #O2O3A3 RCHO + #O2O3K3 ACET + #O2O3K4 MEK + &  
 #O2O3BZ BALD + #O2O3Z1 (HCHO2) + #O2O3Z2 (CCHO2) + &  
 #O2O3Z3 (RCHO2) + #O2O3Z4 (C(C)CO2) + &  
 #O2O3Z5 (C(R)CO2) + #O2O3Z6 (CYCCO2) + &  
 #O2O3Z8 (BZCHO2) + #O2O3OH HO + #O2O3RR RO2-R + &  
 #O2O3RN RO2-N + #O2O3XN RO2-XN + #O2O3NP RO2-NP + &  
 #O2O3RH HO2 + #O2O3R2 R2O2 + #O2O3RS RO2 + &  
 #O2O3Q1 CCO-O2 + #O2O3Q2 C2CO-O2 + #O2O3QS RCO3 + &  
 #O2O3XC XC

!

O2OA) ;OLE2 + O = #O2OARR RO2-R + #O2OARH HO2 + &  
 #O2OARS RO2 + #O2OAA1 HCHO + #O2OAA3 RCHO + &  
 #O2OAK4 MEK + #O2OACO CO + #O2OAXC XC

!

O2N3) ;OLE2 + NO3 = #O2N3N2 NO2 + #O2N3N3 HNO3 + &  
 #O2N3RH HO2 + #O2N3RR RO2-R + #O2N3RN RO2-N + &  
 #O2N3R2 R2O2 + #O2N3RS RO2 + #O2N3A1 HCHO + &  
 #O2N3A2 CCHO + #O2N3A3 RCHO + #O2N3K3 ACET + &  
 #O2N3K4 MEK + #O2N3BZ BALD + #O2N3XC XC

!

O3OH) ;OLE3 + HO = #O3OHRR RO2-R + #O3OHRN RO2-N + &  
 #O3OHRHS RO2 + #O3OHA1 HCHO + #O3OHA2 CCHO + &  
 #O3OHA3 RCHO + #O3OHK3 ACET + #O3OHK4 MEK + &  
 #O3OHBZ BALD + #O3OHXC XC

!

O3O3) ;OLE3 + O3 = #O3O3A1 HCHO + #O3O3A2 CCHO + &  
 #O3O3A3 RCHO + #O3O3K3 ACET + #O3O3K4 MEK + &  
 #O3O3BZ BALD + #O3O3Z1 (HCHO2) + #O3O3Z2 (CCHO2) + &  
 #O3O3Z3 (RCHO2) + #O3O3Z4 (C(C)CO2) + &  
 #O3O3Z5 (C(R)CO2) + #O3O3Z6 (CYCCO2) + &  
 #O3O3Z8 (BZCHO2) + #O3O3OH HO + #O3O3RR RO2-R + &  
 #O3O3RN RO2-N + #O3O3XN RO2-XN + #O3O3NP RO2-NP + &  
 #O3O3RH HO2 + #O3O3R2 R2O2 + #O3O3RS RO2 + &  
 #O3O3Q1 CCO-O2 + #O3O3Q2 C2CO-O2 + #O3O3QS RCO3 + &  
 #O3O3XC XC

!

O3OA) ;OLE3 + O = #O3OARR RO2-R + #O3OARH HO2 + &  
 #O3OARS RO2 + #O3OAA1 HCHO + #O3OAA3 RCHO + &  
 #O3OAK4 MEK + #O3OACO CO + #O3OAXC XC

!

O3N3) ;OLE3 + NO3 = #O3N3N2 NO2 + #O3N3N3 HNO3 + &  
 #O3N3RH HO2 + #O3N3RR RO2-R + #O3N3RN RO2-N + &  
 #O3N3R2 R2O2 + #O3N3RS RO2 + #O3N3A1 HCHO + &  
 #O3N3A2 CCHO + #O3N3A3 RCHO + #O3N3K3 ACET + &  
 #O3N3K4 MEK + #O3N3BZ BALD + #O3N3XC XC

!

! END OF FILE

### A.2 Reactions of Isoprene

! REACTIONS OF ISOPRENE (Condensed - 1)

ISOH) 2.54E-11 -0.81 ;ISOP + HO = #.088 RO2N + #.912 RO2R + &  
                   #.629 HCHO + #.912 ISPD + #.079 R2O2 + &  
                   #1.079 RO2  
!

ISO3) 7.86E-15 3.80 ;ISOP + O3 = #.4 HCHO + #.6 ISPD + #.55 BHCHO2 + &  
                   #.2 CC3O2 + #.2 CC3HO2  
!

ISOA) 3.60E-11 ;ISOP + O = #.75 ISPD + #.25 "C3O3 + &  
                   RCO3 + #2 HCHO + RO2R + RO2"  
!

!ISOA) 3.60E-11 ;ISOP + O = #.75 "ISPD + XC " + #.25 "C3O3 + &  
                   RCO3 + #2 HCHO + RO2R + RO2"  
!

ISN3) 3.03E-12 0.89 ;ISOP + NO3 = #.8 "RCHO + RNO3 + RO2R " + &  
                   #.2 "ISPD + R2O2 + NO2" + RO2  
!

ISN2) 1.50E-19 ;ISOP + NO2 = #.8 "RCHO + RNO3 + RO2R " + &  
                   #.2 "ISPD + R2O2 + NO" + RO2  
!

!

IPOH) 3.36E-11 ;ISPD + HO = #.293 CO + #.252 CCHO + #.126 HCHO + &  
                   #.041 GLY + #.021 RCHO + #.168 MGLY + #.314 MEK + &  
                   #.503 RO2R + #.21 CCO3 + #.288 C3O3 + &  
                   #.21 R2O2 + #.713 RO2 + #.498 RCO3  
!

IPO3) 7.11E-18 ;ISPD + O3 = #.02 CCHO + #.04 HCHO + #.01 GLY + &  
                   #.84 MGLY + #.09 MEK + #.66 BHCHO2 + &  
                   #.09 HOCCHO2 + #.18 HOCCCHO2 + #.06 C2O2CHO + &  
                   #.01 COHC2O2  
!

IPHV) PF=ACROLEIN ;ISPD + HV + #.0036 = #.333 CO + #.067 CCHO + &  
                   #.9 HCHO + #.033 MEK + #.333 HO2 + #.7 RO2R + &  
                   #.267 CCO3 + #.7 C3O3 + #.7 RO2 + &  
                   #.967 RCO3  
!

IPN3) 1.0E-15 ;ISPD + NO3 = #.643 CO + #.282 HCHO + #.85 RNO3 + &  
                   #.357 RCHO + #.925 HO2 + #.075 C3O3 + &  
                   #.075 R2O2 + #.925 RO2 + #.075 RCO3 + #.075 HNO3  
!

ISZ1) 1.0 ;CC3O2 = HO + R2O2 + HCHO + C3O3 + RO2 + &  
                   RCO3  
ISZ2) 1.0 ;CC3HO2 = #.75 RCHO + #.25 ISPD  
!

!ISZ2) 1.0 ;CC3HO2 = #.75 RCHO + #.25 ISPD + #.5 XC  
MAZ1) 1.0 ;C2O2CHO = HO + R2O2 + HCHO + HC2O4 + RO2 + &  
                   RCO3  
M1Z1) 1.0 ;HOCCCHO2 = #.6 HO + #.3 "CCO3 + RCO3" + &  
                   #.3 "RO2R + HCHO + CO + RO2"  
!

M2Z1) 1.0 ;.3 "RO2R + HCHO + CO + RO2" + #.8 XC  
;

!M2Z1) 1.0 ;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + &  
                   #.51 HCHO  
!

M2Z2) 1.0 ;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + #.74 XC + &  
                   #.51 "CO2 + HCHO"  
!

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### A.3 Explicit Reaction Mechanisms for Selected Hydrocarbons

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OH001) 2.500E-12 0.397 0.000 ;C6H6 + HO = #.236 PHEN + #.207 GLY &
+ #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
+ #1.29 XC + #.764 RO2
!
OH033) 1.480E-11 -0.890 0.000 ;BUTD + HO = RO2-R + RO2 + HCHO + RCHO
!
O3033) 1.340E-14 4.537 0.000 ;BUTD + O3 = #.6 HCHO + RCHO + #-1.2 XC &
+ #.4 (HCHO2) + #.6 (CCHO2)
!
N3033) 1.000E-13 0.000 0.000 ;BUTD + NO3 = R2O2 + RO2 + HCHO + RCHO &
+ NO2
!
OA033) 2.100E-11 0.000 0.000 ;BUTD + O = #.4 HO2 + #.5 RCHO + #.5 MEK &
+ #.5 XC
!
OH018) 3.840E-13 0.000 0.000 ;PDCB + HO = #.236 PHEN + #.207 GLY &
+ #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
+ #1.29 XC + #.764 RO2

OH152) 9.640E-12 2.403 0.000 ;PERC + HO = RO2-R + CCHO + RO2
!
OH086) 6.14E-18 1.987 2.000 ;DICM + HO = RO2-R + HCHO + RO2
!
AS1) 6.14E-25 ; AS = AS
CR1) 6.14E-25 ; CRVI = CRVI
!
C1) PF=HCHONEWR ;FORM + HV = #2 HO2 + CO
C2) PF=HCHONEWM ;FORM + HV = H2 + CO
C3) 1.125E-12 -1.288 2.00 ;FORM + HO = HO2 + CO + H2O
C4) 9.7E-15, -1.242 ;FORM + HO2 = HOCOO
C9) 2.8E-12, 5.00 ;FORM + NO3 = HNO3 + HO2 + CO
!
C10) 5.55E-12, -0.618 ;ALD + HO = CCO-O2 + H2O + RCO3
C11A) PF=CCHOR ;ALD + HV = CO + HO2 + HCHO + RO2-R + RO2
C12) 1.4E-12, 3.696 ;ALD + NO3 = HNO3 + CCO-O2 + RCO3
!
OH091) 5.560E-13 -1.057 2.000 ;ETOH + HO = #.1 RO2-R + #.9 HO2 &
+ #.156 HCHO + #.922 CCHO + #.1 RO2
!
OH108) 6.129E-13 -0.914 2.000 ;MTBE + HO = #.02 RO2-N + #.98 RO2-R &
+ #.37 R2O2 + #.39 HCHO + #.41 MEK + #2.87 XC &
+ #1.37 RO2
!
!      END OF FILE

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